Analysis of electron inelastic scattering in solids over wide energy range and its application to surface chemical analysis

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1. Introduction
   - physical parameters for surface analysis ; IMFP, EAL, MED, ID, EDDF
2. Calculations and analysis of IMFPs
   - evaluation of energy-loss function
   - calculations with relativistic full Penn algorithm
   - Fano Plots : relativistic modified Bethe equation
   - comparison of IMFPs from EPES experiments
3. Applications to surface analysis
   - MEDs for HAXPES
4. Summary

1. Introduction

- Parameters for electron attenuation in solids

  - inelastic mean free path (IMFP) : nm
  - stopping power (SP) : eV/nm (energy loss)

  → **Bulk quantity** (fundamental)

  - mean escape depth (MED) : nm (SS)
  - effective attenuation length (EAL) : nm (thickness)
  - information depth (ID) : nm

  → **From IMFPs**
  experimental conditions ; probe , emission angle, etc)

calculated from emission depth distribution function (EDDF)

: escape probability of signal electrons emitted at depth z

IMFPs

definition: average distance that an electron with a given energy travels between successive inelastic collisions

- most basic material parameter for describing the surface sensitivity of AES, XPS and other surface electron spectroscopies.
- growing interest in XPS and related experiments performed with X-rays of much higher energies for both scientific and industrial purposes. (up to 30keV)
- a need for IMFPs at higher energy region in transmission electron microscopy. (up to 200 or 300 KeV)

We have extended IMFP calculations **over 10 eV to 200 keV using relativistic full Penn algorithm (FPA)** from ELFs **for 41 elemental solids and 30 compound semiconductors.**

2. Calculation of IMFPs from optical data
- IMFP calculation with relativistic full Penn algorithm

:Relativistic DCS (< 0.5 MeV; Fernandez-Varea)

$$\frac{d^2\sigma}{d\omega dq} = \frac{d^2\sigma_L}{d\omega dq} + \frac{d^2\sigma_T}{d\omega dq} \approx \frac{d^2\sigma_L}{d\omega dq} = \frac{2}{\pi N v^2} \mathrm{Im}\left(\frac{-1}{\varepsilon(q,\omega)}\right)\frac{1}{q}$$

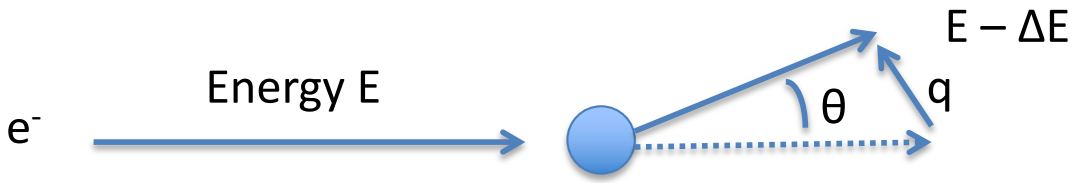
: Probability $P(T,\omega)$ for energy loss per unit distance traveled by an electron with relativistic kinetic energy T.

$$p(T,\omega) = \frac{\left(1+T/c^2\right)^2}{1+T/\left(2c^2\right)}\frac{1}{\pi T}\int_{q_-}^{q_+}\frac{dq}{q}\mathrm{Im}\left[\frac{-1}{\varepsilon(q,\omega)}\right]$$

$$q_\pm = \sqrt{T\left(2+T/c^2\right)} \pm \sqrt{(T-\omega)\left(2+(T-\omega)/c^2\right)}$$

$$\lambda(T) = 1/\int_0^{\omega_{\max}} p(T,\omega)\ d\omega$$

Full Penn Algorithm for ELF calculation



experimental optical data

: optical constants

: atomic scattering factors

$$\mathrm{Im}\left[-1/\varepsilon(\Delta E)\right]$$

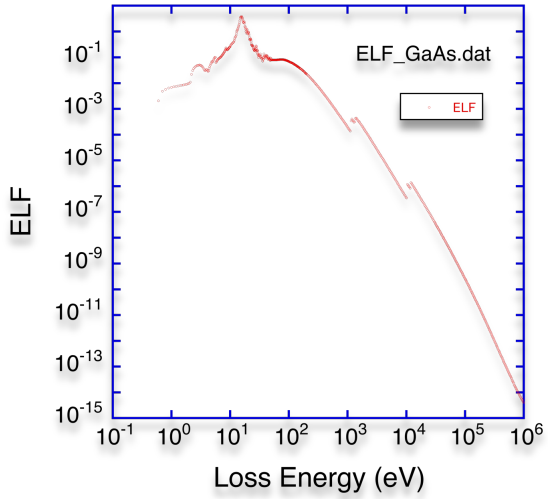
Energy dependence; q=0

- Optical ELF

$$\mathrm{Im}\left[\frac{-1}{\varepsilon(\Delta E, q)}\right]$$

Full Penn algorithm

Ex. Optical ELF of GaAs



- q dependence : $q > 0$

FPA: Lindhard model dielectric function (RPA)

$$\mathrm{Im}\left[\frac{-1}{\varepsilon(q,\omega)}\right] = \int_0^\infty d\omega_p g(\omega_p)\,\mathrm{Im}\left[\frac{-1}{\varepsilon^L(q,\omega;\omega_p)}\right]$$

$$g(\omega) = \frac{2}{\pi\omega}\mathrm{Im}\left[\frac{-1}{\varepsilon(\omega)}\right]$$

← optical ELF

Conditions for IMFP calculations

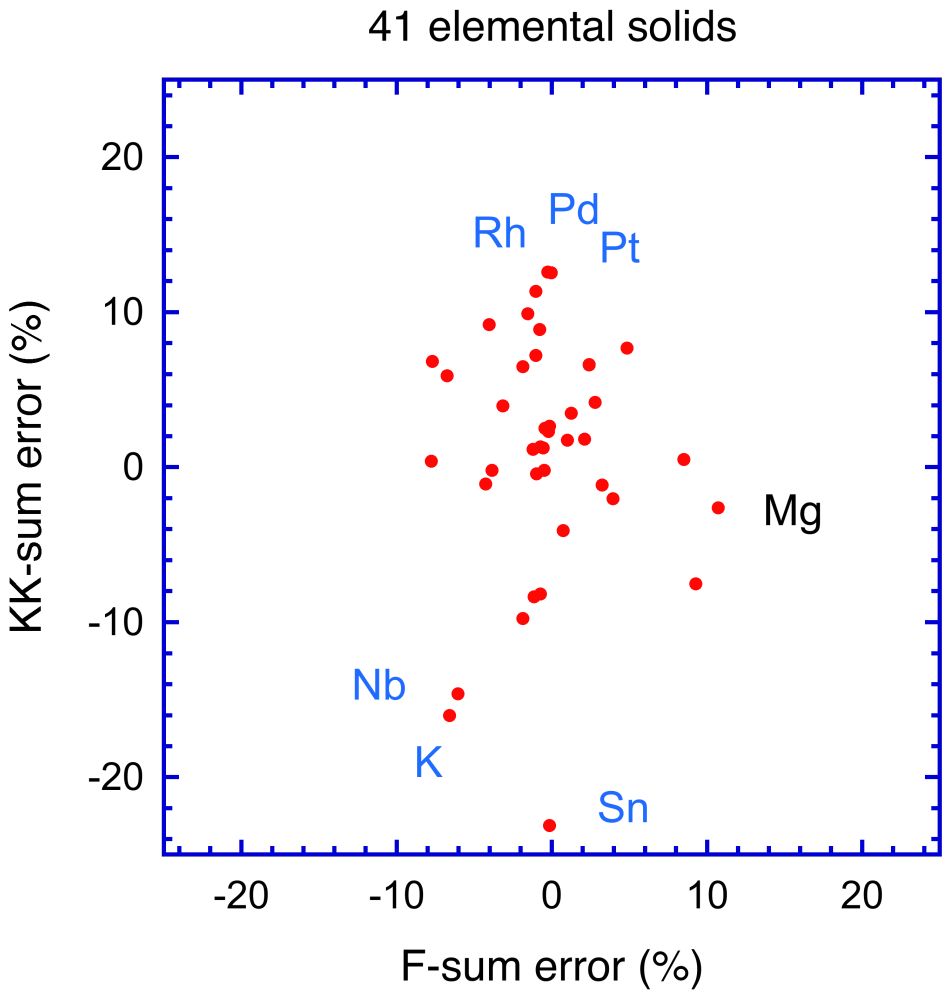
Energy range for IMFP calculations: **10 eV to 200 keV**
- calculated at equal intervals on a logarithmic energy scale corresponding to increases of 10 %.

Energy range of **optical ELFs** for materials**: 0.1 eV - 1MeV**

- 41 elemental solids
Li, Be, diamond, graphite, glassy carbon, Na, Mg, Al, Si, K, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Ge, Y, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Cs, Gd, Tb, Dy, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Bi.

-30 compound semiconductors
AgBr, AgCl, AgI, AlAs, AlN, AlSb, BN, BN(hex), CdS, CdSe, CdSe(hex), CdTe, GaAs, GaN, GaP, GaSb, GaSe, InAs, InP, InSb, PbS, PbSe, PbTe, SiC, SiC(hex), SnTe, ZnS, ZnS(hex), ZnSe, ZnTe

Evaluation of ELFs (0 - 1MeV) : elemental solids



: OCs from HOC I, II, III by Palik (<30 eV)
>100 eV atomic scattering factors (Henke)

- **F-sum : evaluate the ELF at high energy region**
- **KK-sum :evaluate the ELFs under 100 eV**

- the sum-rule errors for K and Nb are both of the same sign (negative in each case), indicating that their ELFs are systematically too small and thus their calculated IMFPs will be too large.

- For 34 of our 41 elemental solids, the f-sum-rule and KK-sum rule errors are both less than 10 %.

ELFs : compound semiconductor

·Experimental ELF (optical constants) are lacking over 10 eV.

- Optical constants and ELFs for 30 compound semiconductors were calculated with **FEFF8.2 and WIEN2K in 0.1 eV – 1 MeV**.

FEFF: Automated program to calculate the X-ray absorption spectra based on an ab initio all-electron, real space relativistic Green's function formalism
→ Available for inner-shell electron excitation

WIEN2K: Program package to perform the electron structure calculation based on density functional theory using full potential and linearized augmented plane wave method
→Available for valence electron excitation

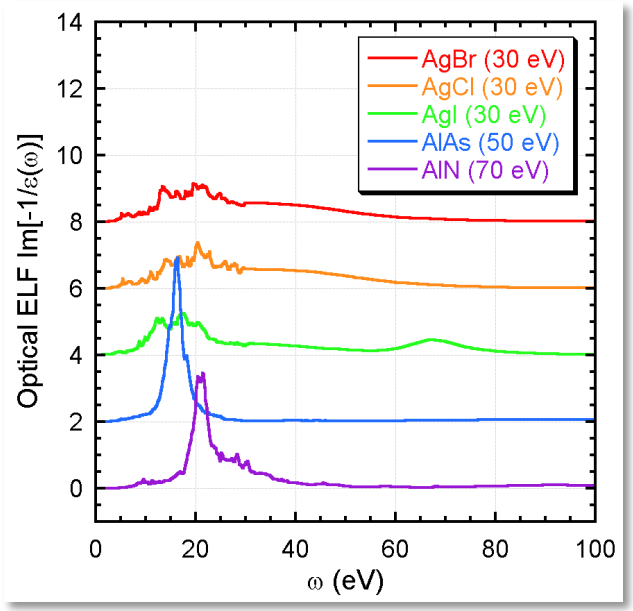
- Space group and cell parameters : ex. AgBr , F m -3 m, a = 5.775

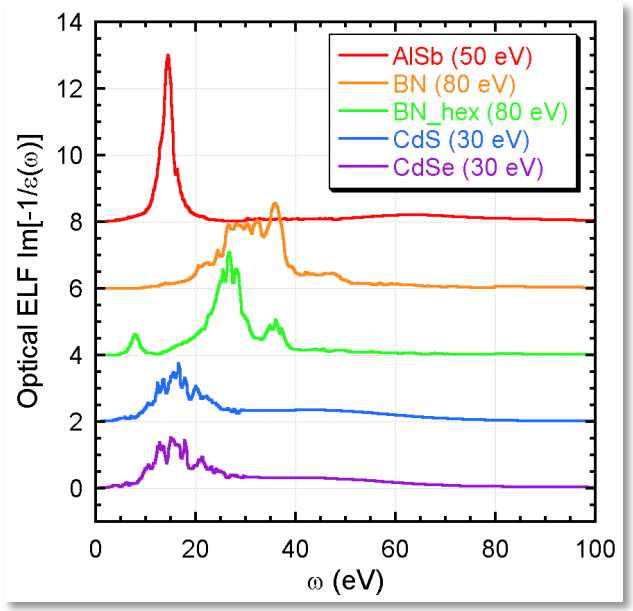
List of 30 semiconductors calculated

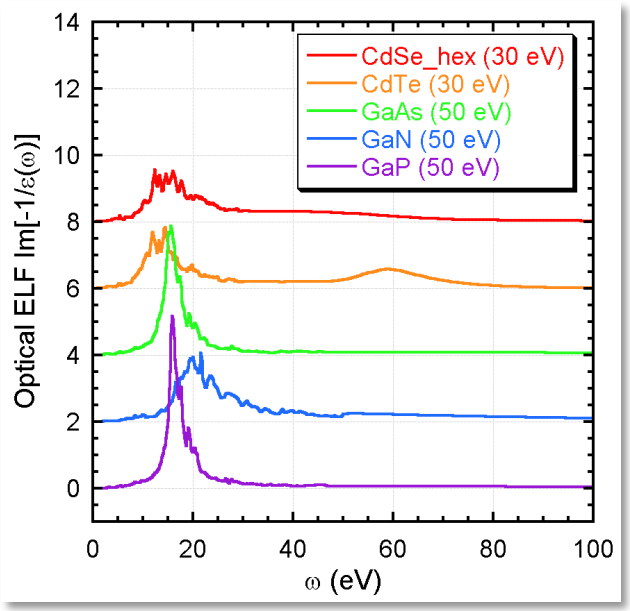
Material	Space Group	Cell parameter (angstrom or degree)
AgBr	F m -3 m	a = 5.775
AgCl	F m -3 m	a = 5.543
AgI	P 63 m c	a = 4.5856 c = 7.49 g = 120
AlAs	F -4 3 m	a = 5.6605
AlN	P 63 m c	a = 3.11 c = 4.98 g = 120
AlSb	F -4 3 m	a = 6.135
BN	F -4 3 m	a = 3.6159
BN_hex	P 63 /mmc	a = 2.5045 c = 6.606 g = 120
CdS	P 63 m c	a = 4.142 c = 6.724 g = 120
CdSe	F -4 3 m	a = 6.04
CdSe_hex	P 63 m c	a = 4.299 c = 7.01 g = 120
CdTe	F -4 3 m	a = 6.482
GaAs	F -4 3 m	a = 5.6532

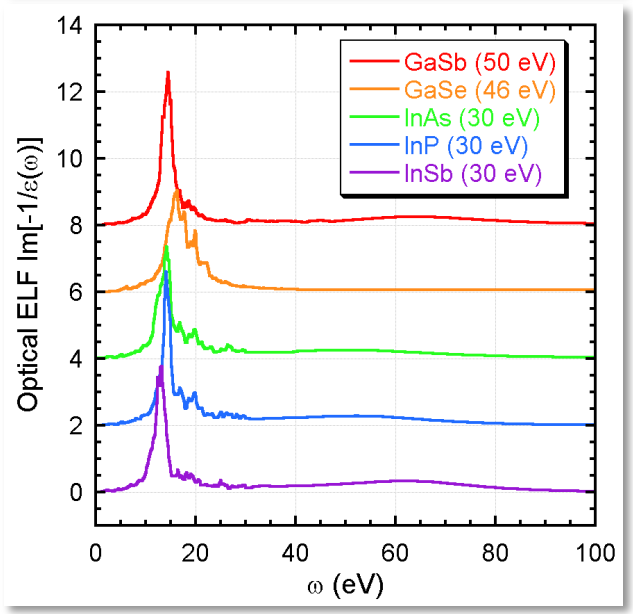
Material	Space Group	Cell parameter (angstrom or degree)
GaN	P 63 m c	a = 3.1891 c = 5.1855 g = 120
GaP	F -4 3 m	a = 5.4508
GaSb	F -4 3 m	a = 6.0959
GaSe	P 63 /mmc	a = 3.75 c = 15.995 g = 120
InAs	F -4 3 m	a = 6.0577
InP	F -4 3 m	a = 5.8687
InSb	F -4 3 m	a = 6.4794
PbS	F m -3 m	a = 5.9315
PbSe	F m -3 m	a = 6.1213
PbTe	F m -3 m	a = 6.4541
SiC	F -4 3 m	a = 4.3581
SiC_hex	P 63 m c	a = 3.076 c = 5.048 g = 120
SnTe	F m -3 m	a = 6.323
ZnS	F -4 3 m	a = 5.4102
ZnS_hex	P 63 m c	a = 3.822 c = 6.26 g = 120
ZnSe	F -4 3 m	a = 5.6692
ZnTe	F -4 3 m	a = 6.1026

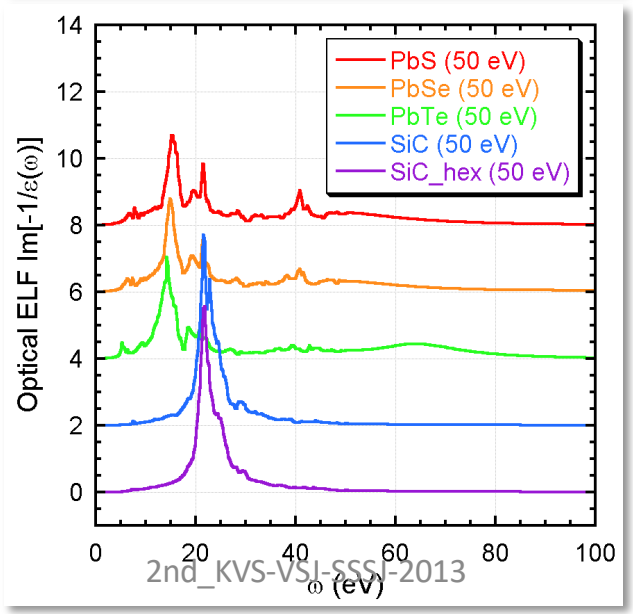
Calculated results of ELFs for 30 compounds: 0 -100 eV

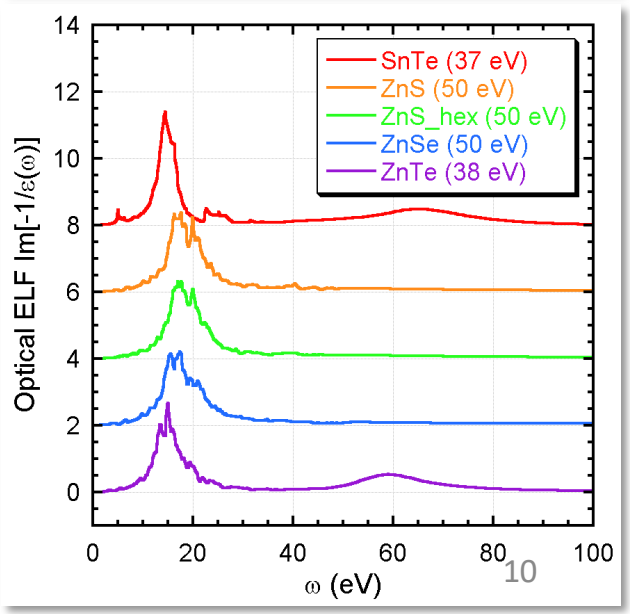




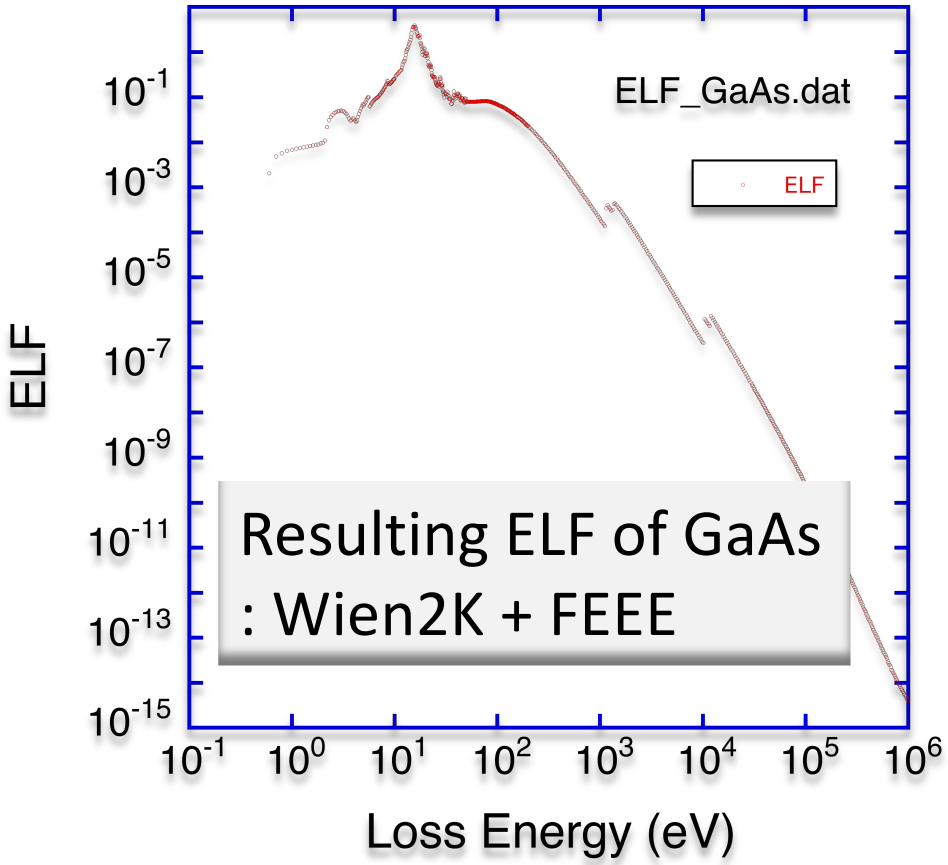






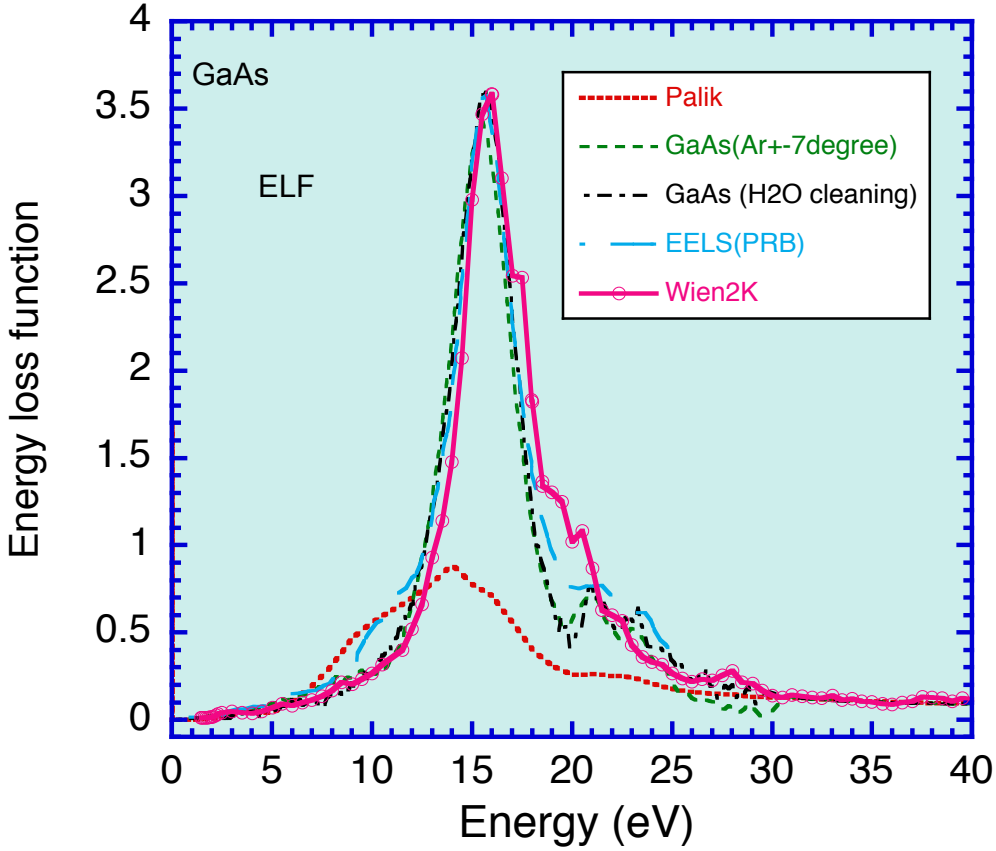


ELF for GaAs



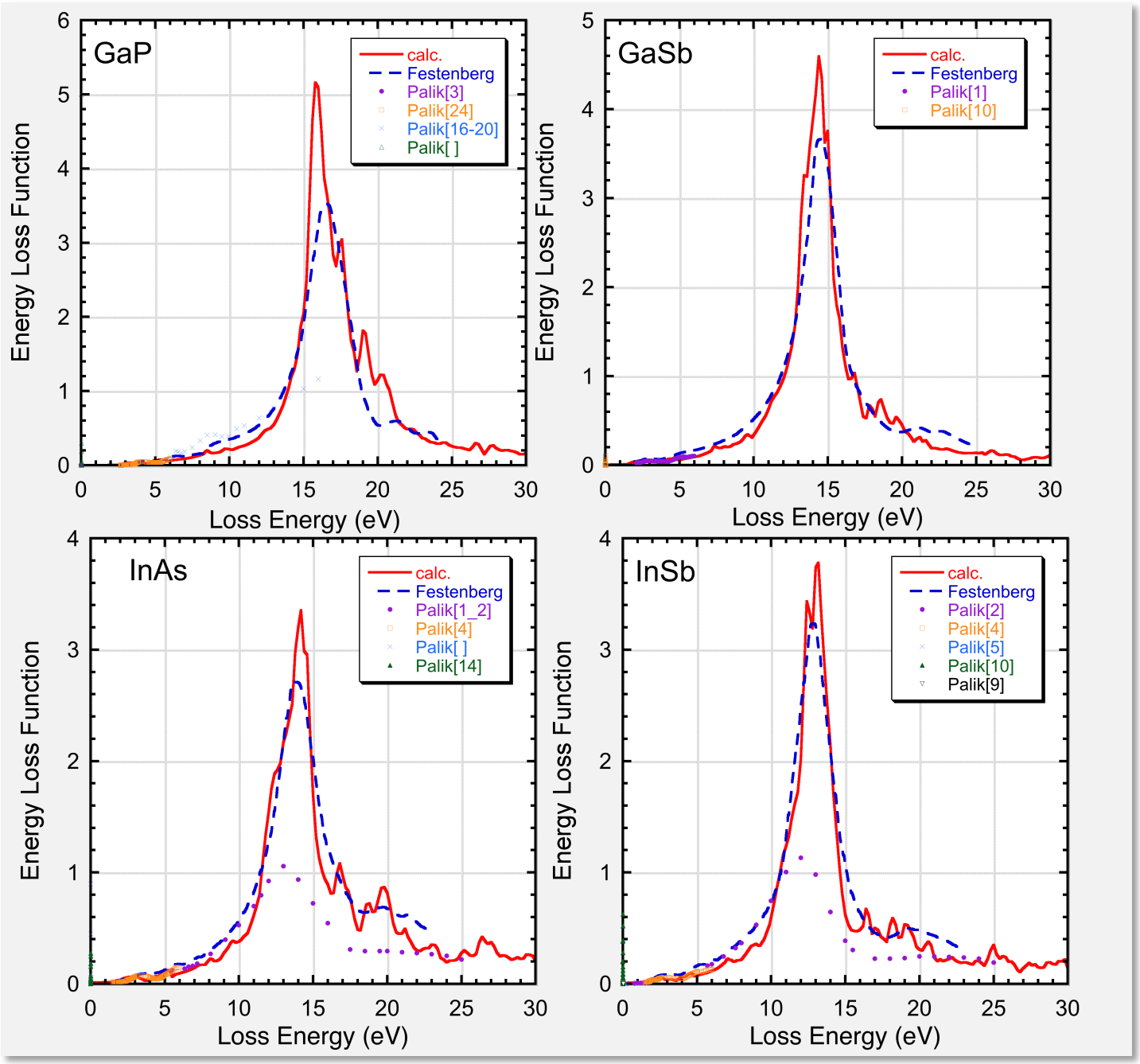
Resulting ELF of GaAs
: Wien2K + FEEE

Comparison of ELFs from REELS



:Theoretical calculations (DFT: Wien2K) gave excellent results for ELF of GaAs !

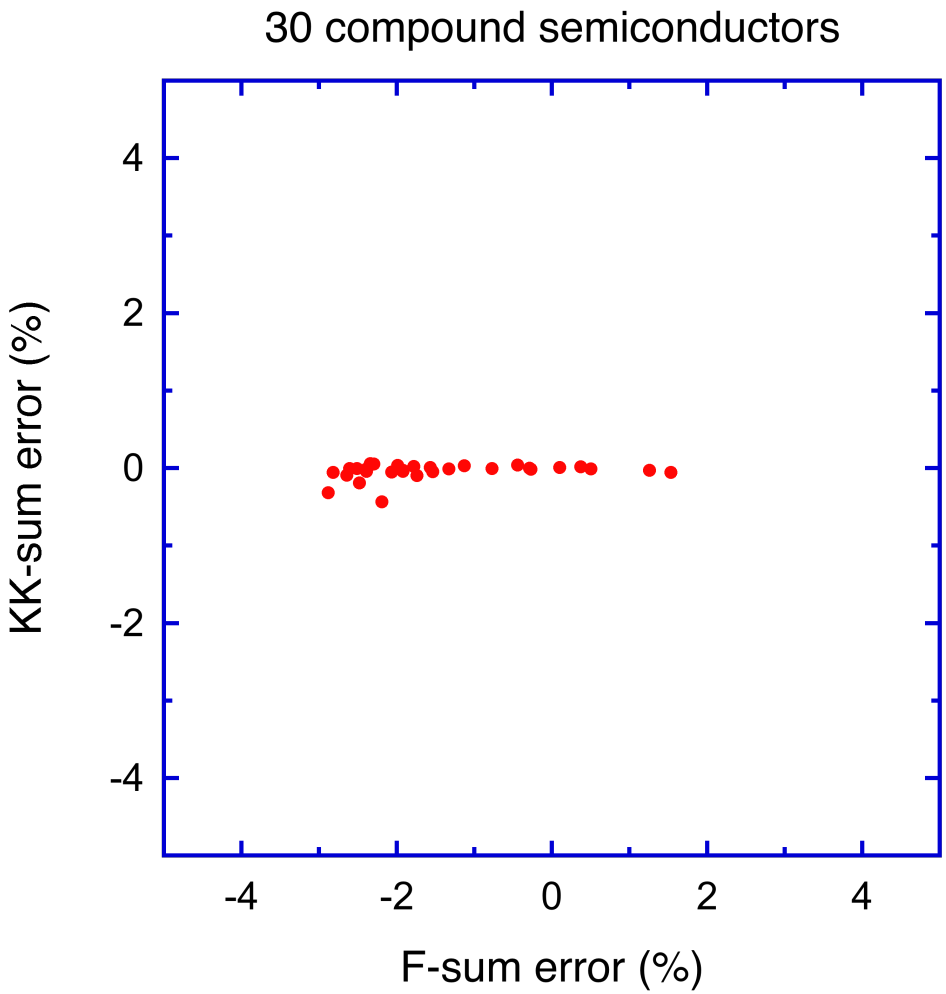
Comparison of ELFs with Palik and TEM-EELS data



: good agreement
Wien2k – TEM (by Festenberg)

: poor >10 eV (InAs,InSb)
Wien2k – Palik data

Evaluation of ELFs : 30 compound semiconductors



KK-sum rule < 0.5%
F-sum rule < 3%

:Wien2K and FEFF code gave excellent OCs or ELFs for compound semiconductors !

- plan to calculate optical ELFs for inorganic compound to make a databse
  (include wide band gap materials)

Relativistic M. Bethe eq. and Fano Plot

$$\sigma_{tot} = \frac{4\pi a_0{}^2 z^2}{mv^2/2R}\left\{M_{tot}^2\left[\ln\left(\frac{4c_{tot}}{R}\frac{mv^2}{2}\right)-\ln\left(1-B^2\right)-B^2\right]\right\} \qquad B=\frac{v}{c}$$

Relativistic Bethe equation by Inokuti

Non-relativistic Bethe equation

$$\sigma_{tot}^{non-rel} = \frac{4\pi a_0{}^2 z^2}{E/R}\left\{M_{tot}^2\left[\ln\left(\frac{4c_{tot}E}{R}\right)\right]+\frac{g_n}{E/R}+O\left(\frac{h_n}{E^2}\right)\right\}$$

$$\lambda^{non-rel} = \frac{E}{E_p{}^2\left\{\beta\ln(\gamma E)-C/E+D/E^2\right\}} \quad (\text{nm})$$

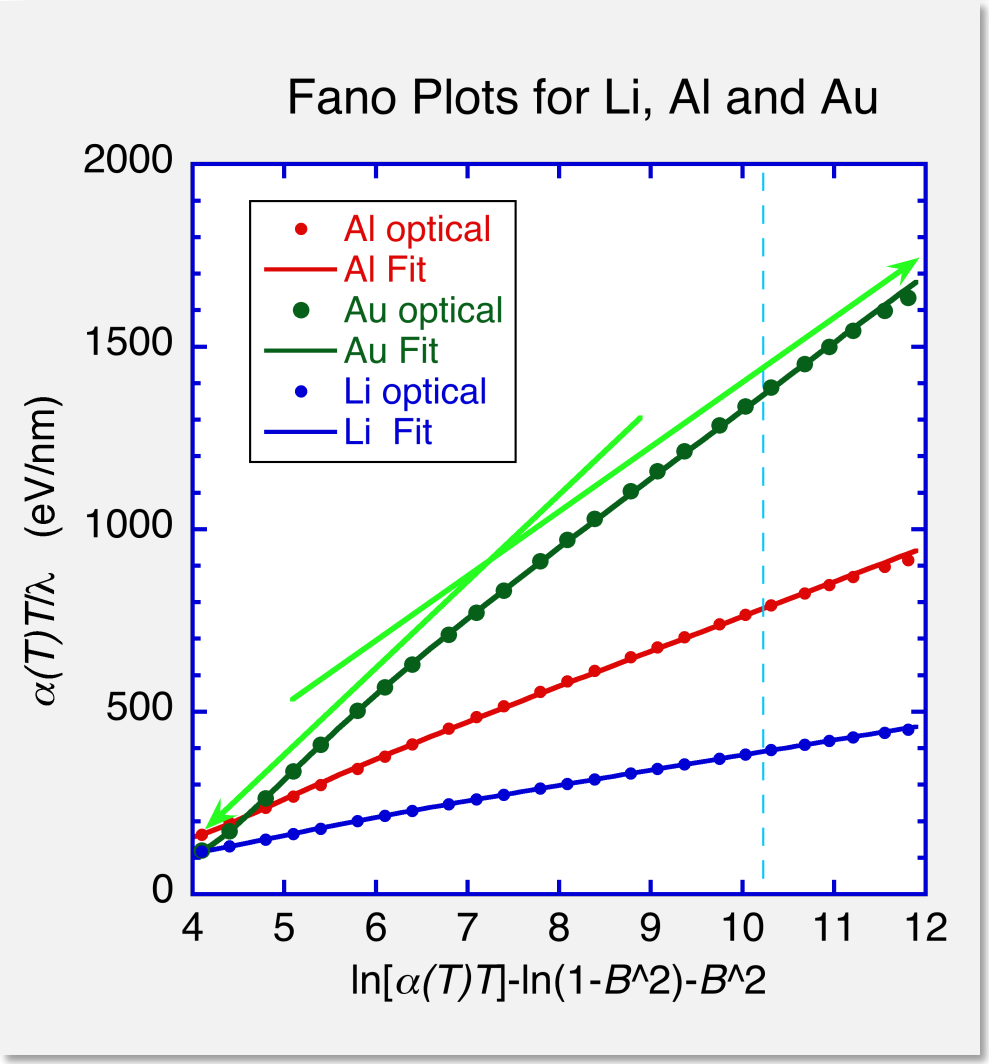
$$\lambda = \frac{\alpha(T)T}{E_p{}^2\left\{\beta\left[\ln\left(\gamma\alpha(T)T\right)-\ln\left(1-B^2\right)-B^2\right]-C/T+D/T^2\right\}} \quad (\text{nm})$$

$$\alpha(T) = \frac{1+T/\left(2m_ec^2\right)}{\left[1+T/\left(m_ec^2\right)\right]^2}$$

Relativistic Fano plot : $\alpha(T)T/\lambda \quad vs. \quad \left[\ln\left(\alpha(T)T\right)-\ln\left(1-B^2\right)-B^2\right]$

Straight line at high energy region : γ = slope

Fano plots and Curve fits for 3 elemental solids



Solid circles: calculated from IMFPs (rel. FPA method)

Solid lines: Fit with Rel. mod. Bethe equation

Energy range: 50 eV – 200 keV

RMS differences (%)

Li : 0.43

Al : 0.98

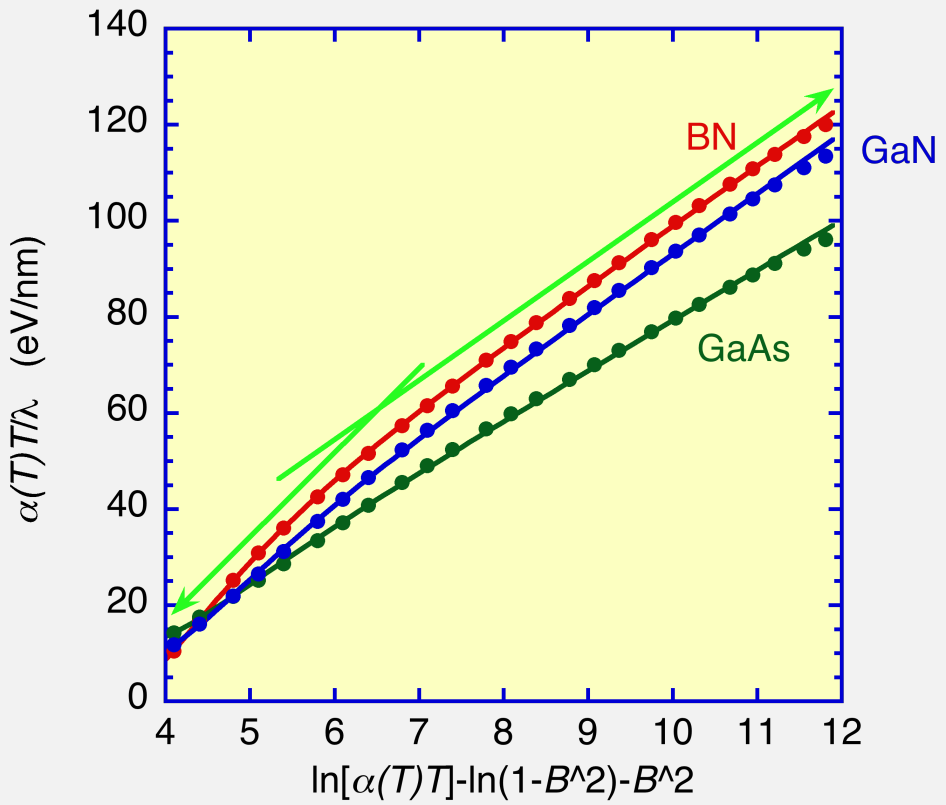
Au : 0.59

Average of RMS (%) for 41 elemental solids

0.82% (0.4 – 1.4 %)

$$\frac{\alpha(T)T}{\lambda} = E_p^{\,2}\left\{\beta\left[\ln\left(\gamma\alpha(T)T\right) - \ln\left(1-B^2\right) - B^2\right] - C/T + D/T^2\right\} \quad \text{(nm/eV)}$$

Fano plots and Curve fits for 3 semiconductiors



Solid circles: calculated from IMFPs (rel. FPA method)

Solid lines: Fit with Rel. mod. Bethe equation

Energy range: 50 eV – 200 keV

RMS differnces (%)

BN : 0.58

GaN : 1.1

GaAs : 1.1

Average of RMS (%) for 30 compounds

0.74 % (0.4 – 1.1 %)

$$\frac{\alpha(T)T}{\lambda} = E_p^{\,2}\left\{\beta\left[\ln\left(\gamma\alpha(T)T\right) - \ln\left(1-B^2\right) - B^2\right] - C/T + D/T^2\right\} \quad \text{(nm/eV)}$$

Relativistic TPP-2M equation

$$\lambda = \frac{\alpha(T)T}{E_p^{\,2}\left\{\beta\left[\ln\left(\gamma\alpha(T)T\right) - \ln\left(1-B^2\right) - B^2\right] - C/T + D/T^2\right\}} \quad \text{(nm)}$$

$$\beta = -1.0 + 9.44/\left(E_p^2 + E_g^2\right)^{0.5} + 0.69\rho^{0.1} \qquad (\mathrm{eV^{-1}nm^{-1}})$$

$$\gamma = 0.191\rho^{-0.5} \qquad (\mathrm{eV^{-1}})$$

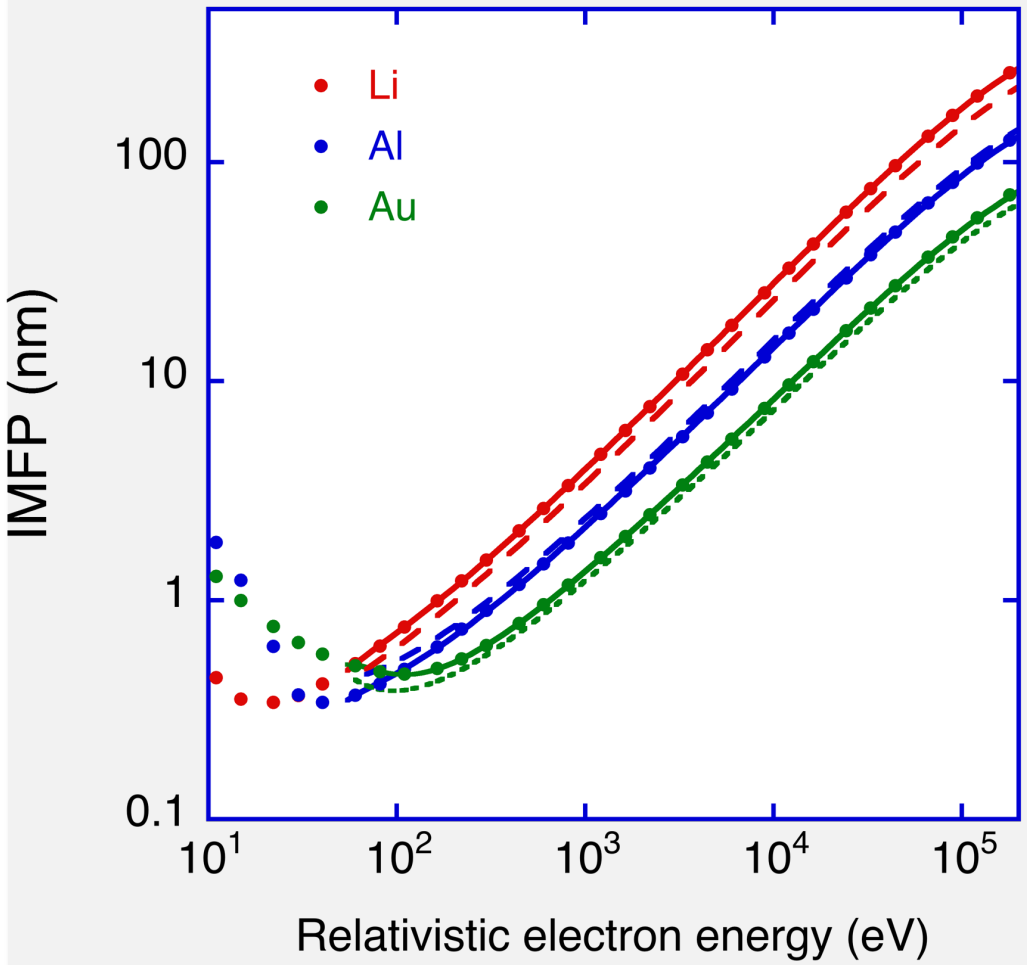
$$C = 19.7 - 9.1U \qquad (\mathrm{nm^{-1}})$$

$$D = 534 - 208U \qquad (\mathrm{eVnm^{-1}})$$

$$\alpha(T) = \frac{1 + T/\left(2m_e c^2\right)}{\left[1 + T/\left(m_e c^2\right)\right]^2}$$

$$B = \frac{v}{c}$$

Comparison of IMFPs with rel. TPP-2M for elemental solids



Solid circles: calculated with rel. FPA
Solid lines: Fit with Rel. M. Bethe eq.
Dashed lines: rel. TPP-2M

Energy range: 50 eV – 200 keV

RMS differences (%) for rel. TPP-2M

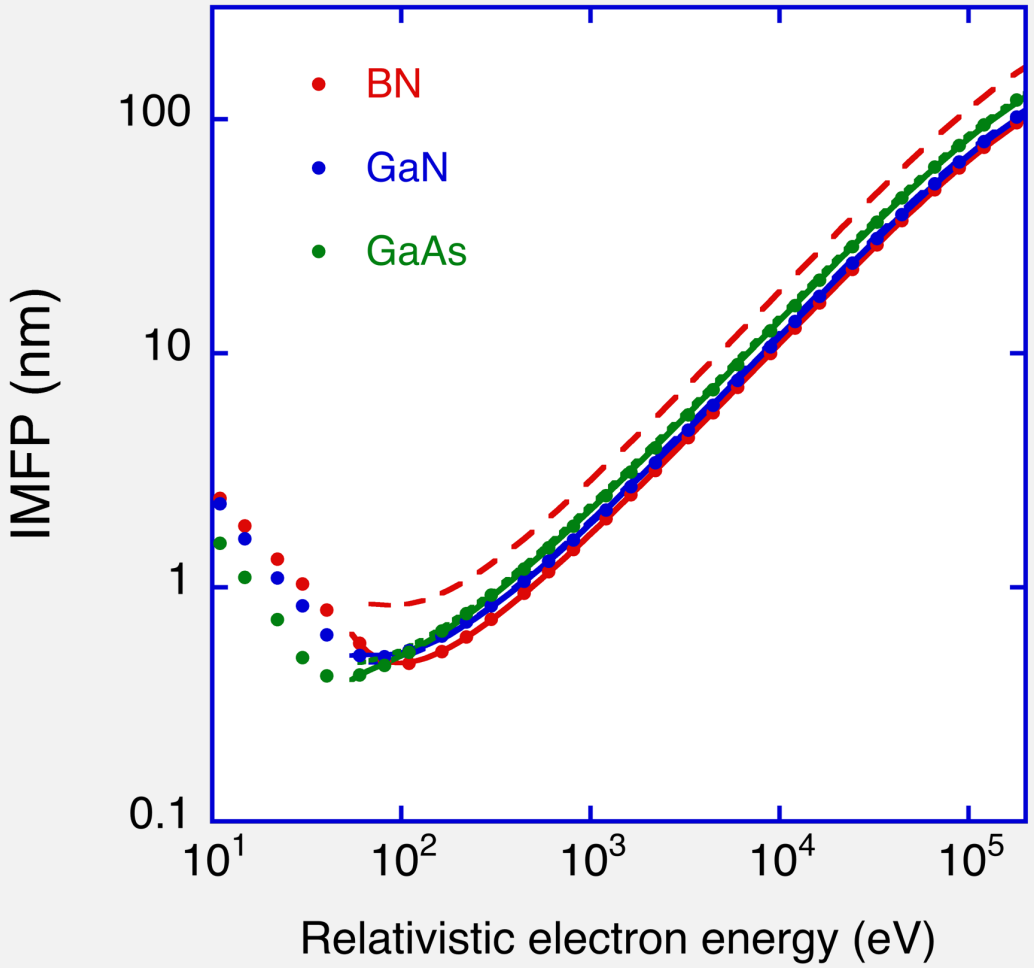
Li	: 15.5
Al	: 10.2
Au	: 11.4

$$RMS = 100 \times \sqrt{\sum_{i=1}^{n} \left(\frac{\lambda_{fit}(E_i) - \lambda(E_i)}{\lambda(E_i)} \right)^2 \Big/ n}$$

Average of RMS (%) for 41 elemental solids

➔ 11.9 % (8.9% ; except for diamond, graphite, Cs)

Comparison of IMFPs with rel TPP-2M for 3 compounds



Solid circles: calculated with rel. FPA
Solid lines: Fit with Rel. M. Bethe eq.
Dotted lines: rel. TPP-2M

Energy range: 50 eV – 200 keV

RMS differences (%) for rel. TPP-2M

BN	: 68.6
GaN	: 3.4
GaAs	: 5.0

Average of RMS (%) for 30 compound semiconductors

11.7 % (2.4 – 69 %)

8.8 % (except BN)

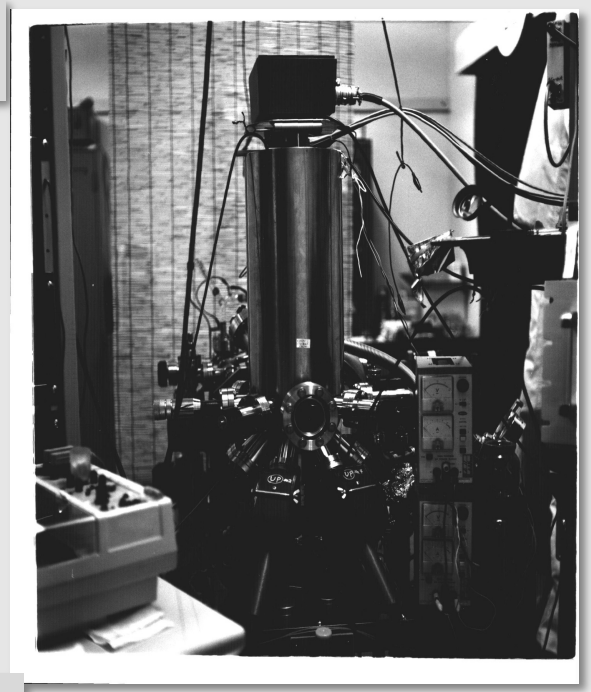
Comparison of IMFPs from EPES experiments

: to know the reliability of IMFPs calculated from ELFs with Penn algorithm (optical IMFP) and from TPP-2M.

- determine IMFPs for **Ag, Au, Cr, Cu, Fe, Ga, C (Graphite) , Mo, Pt, Si, Ta, W and Zn** in the **50 - 5000 eV** energy range from **backscattered elastic-peak intensities (EPIs) using Ni-reference**

- compare with the corresponding calculated IMFPs (optical and TPP-2M).

Measurements of EPIs by absolute CMA



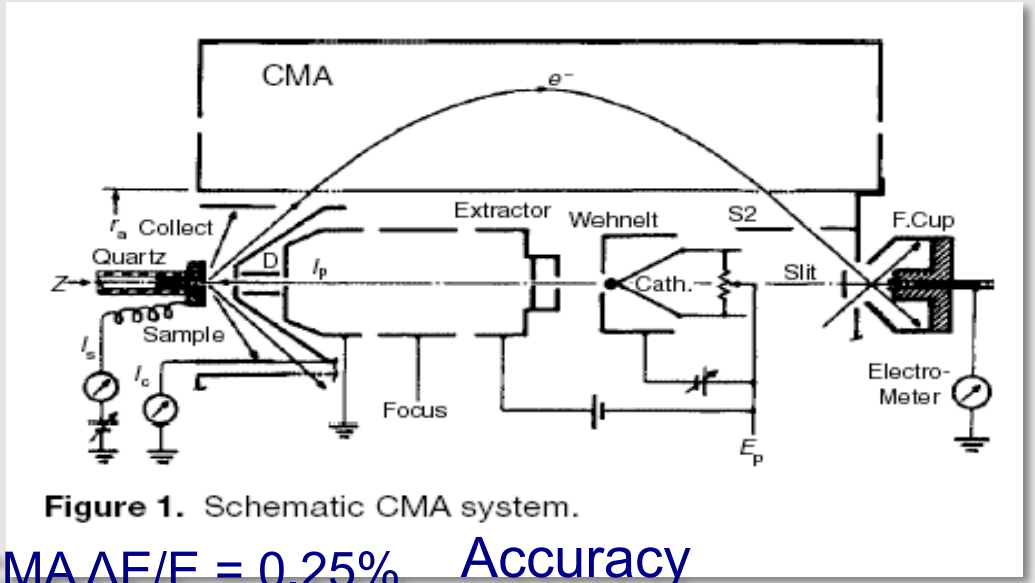


Figure 1. Schematic CMA system.

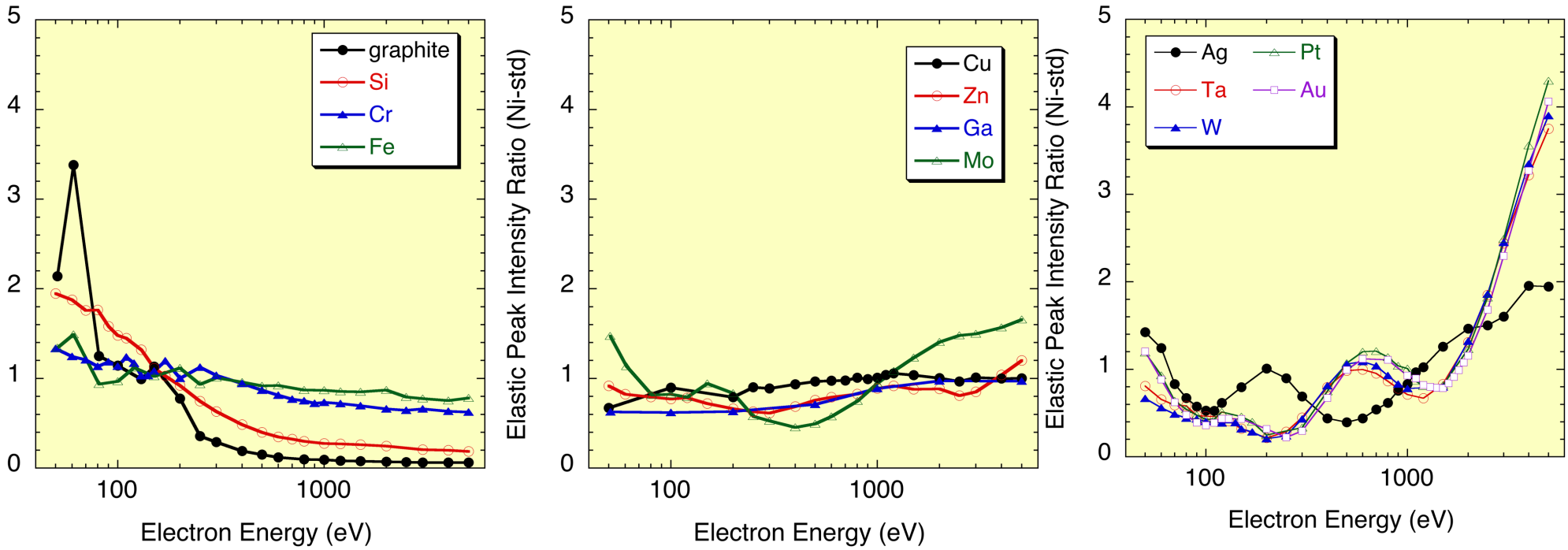
CMA ΔE/E = 0.25%

Accuracy
± 0.01% (primary beam energy)
± 0.5% (Auger spectra)

Measurement of Elastic Peak Intensity
Energy range : 1 - 5,000 eV
(50 - 5,000 eV)
Instrument: Absolute Auger Spectrometer
-detection angle (42.3± 6°)

Primary beam: 1μA
Detector: Faraday cup

Measured elastic peak intensity ratios (Ni-std) as a function of electron energy



Calculation of EPI with MC method

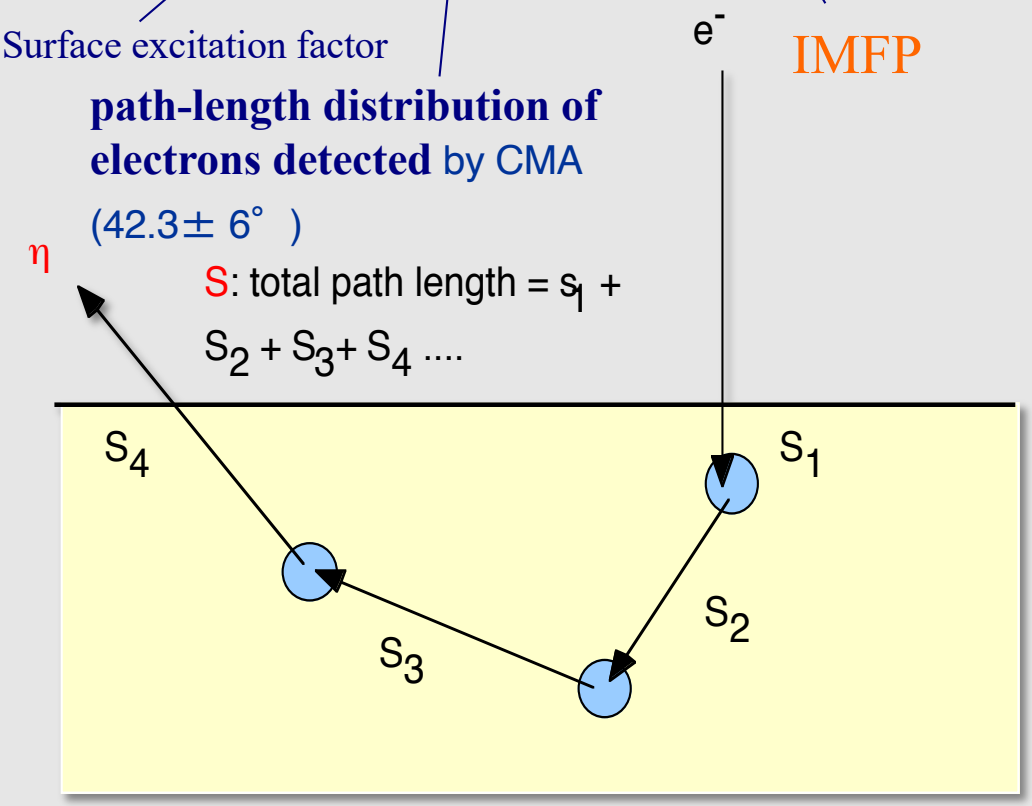
$$I = G_t \times f_s \times \int_0^\infty \left(\frac{d\eta}{dS}\right) / N_0 \exp\left(-\frac{S}{\lambda}\right) dS$$

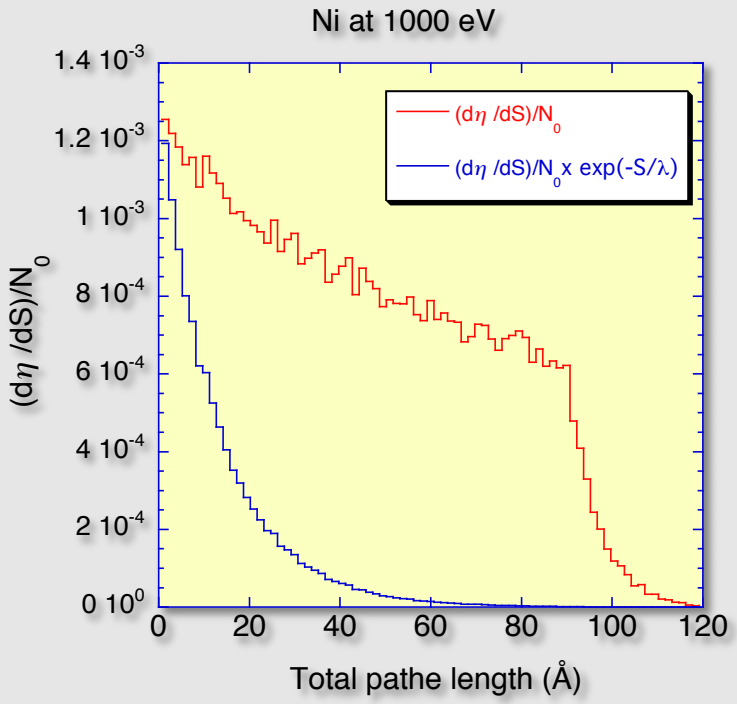
Surface excitation factor

IMFP

path-length distribution of electrons detected by CMA

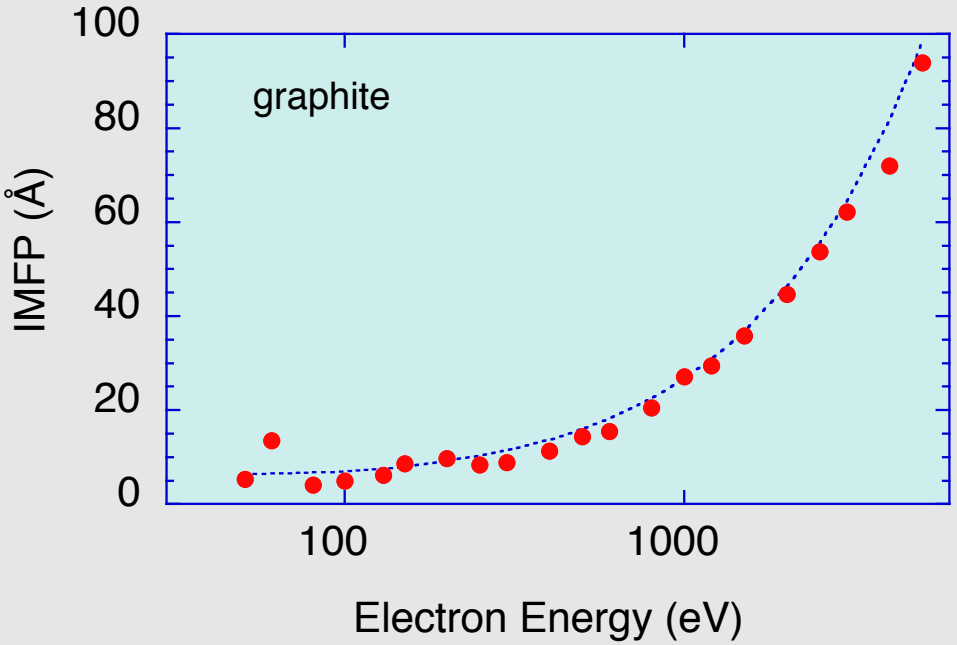
(42.3± 6°)

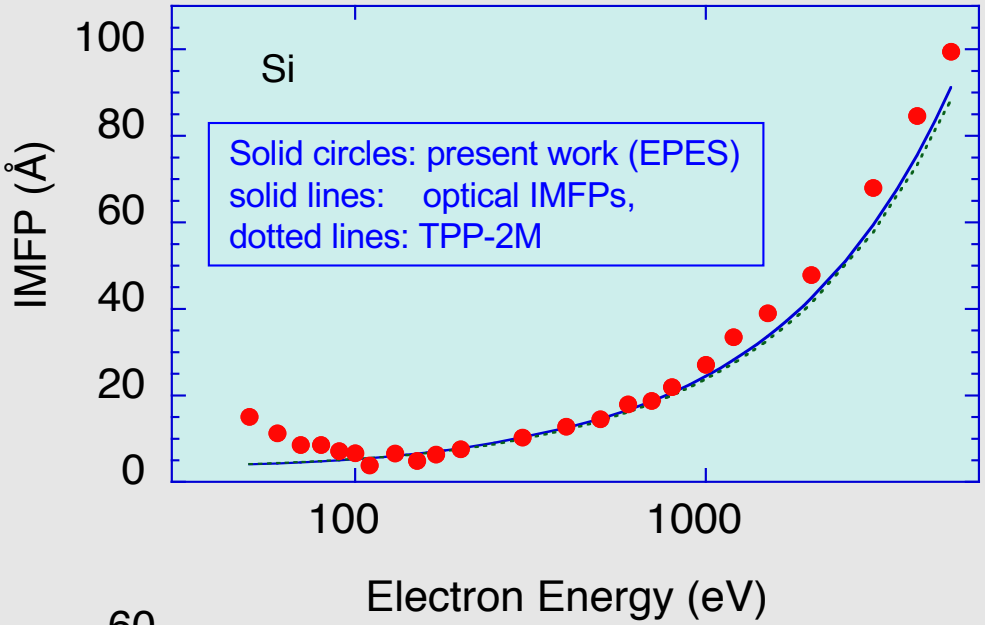


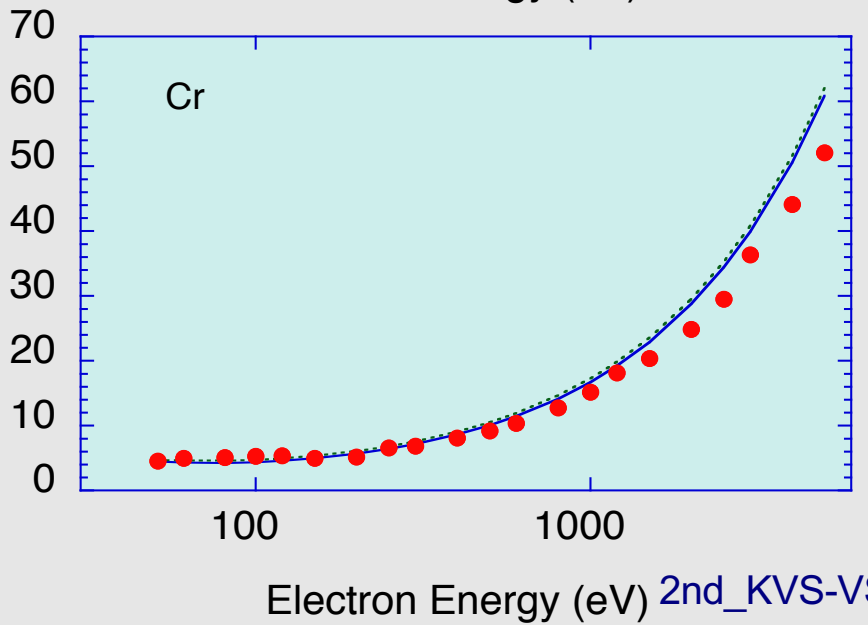


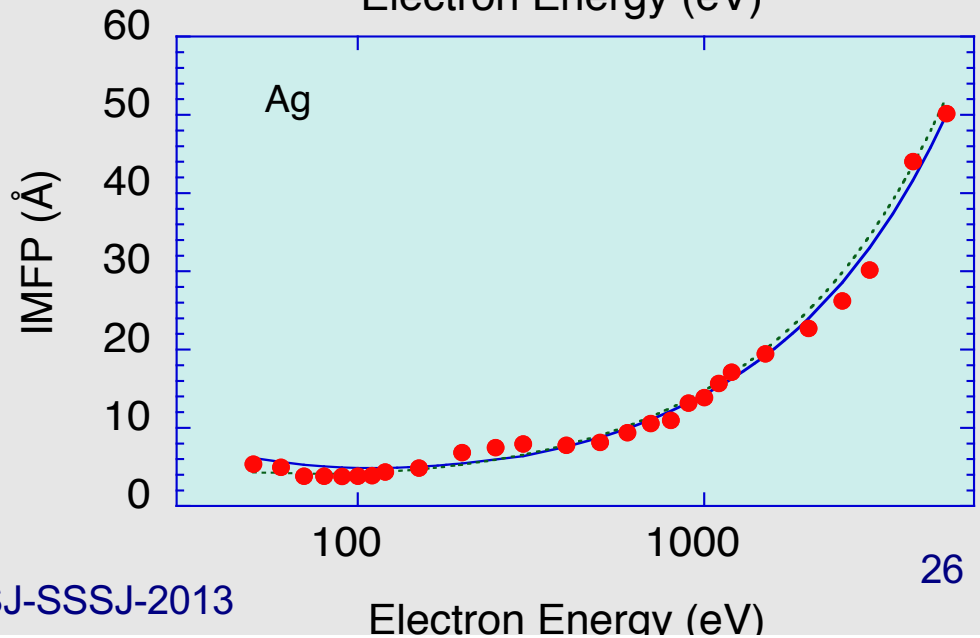
:Elastic scattering cross section
TFD or DHF potential

IMFPs determined from EPI ratios



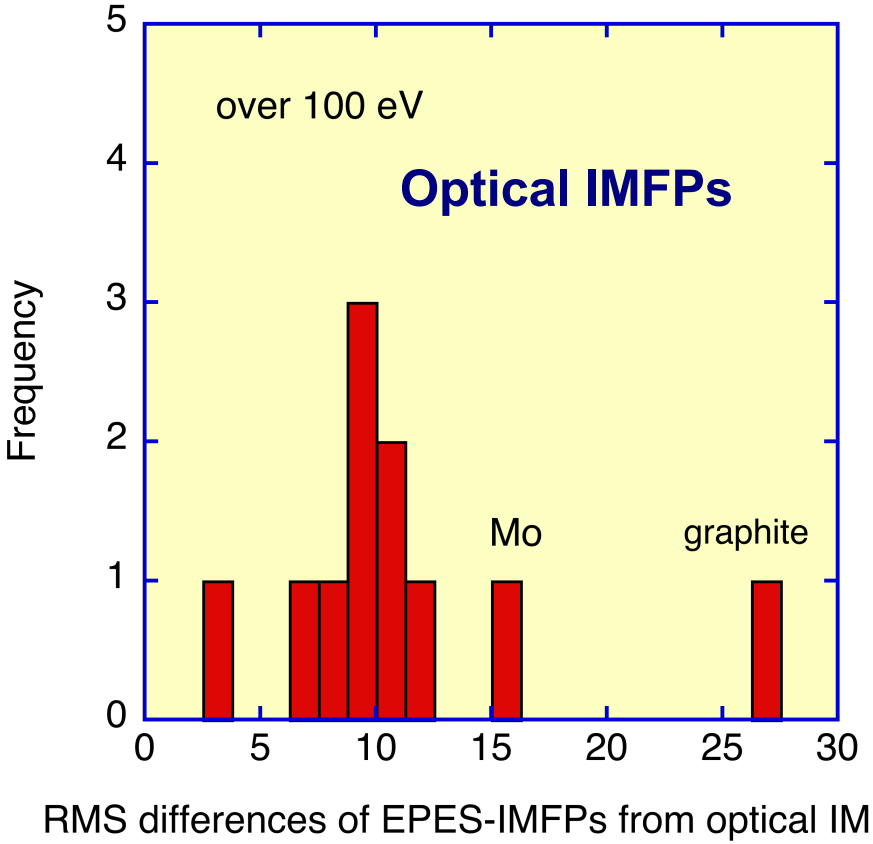


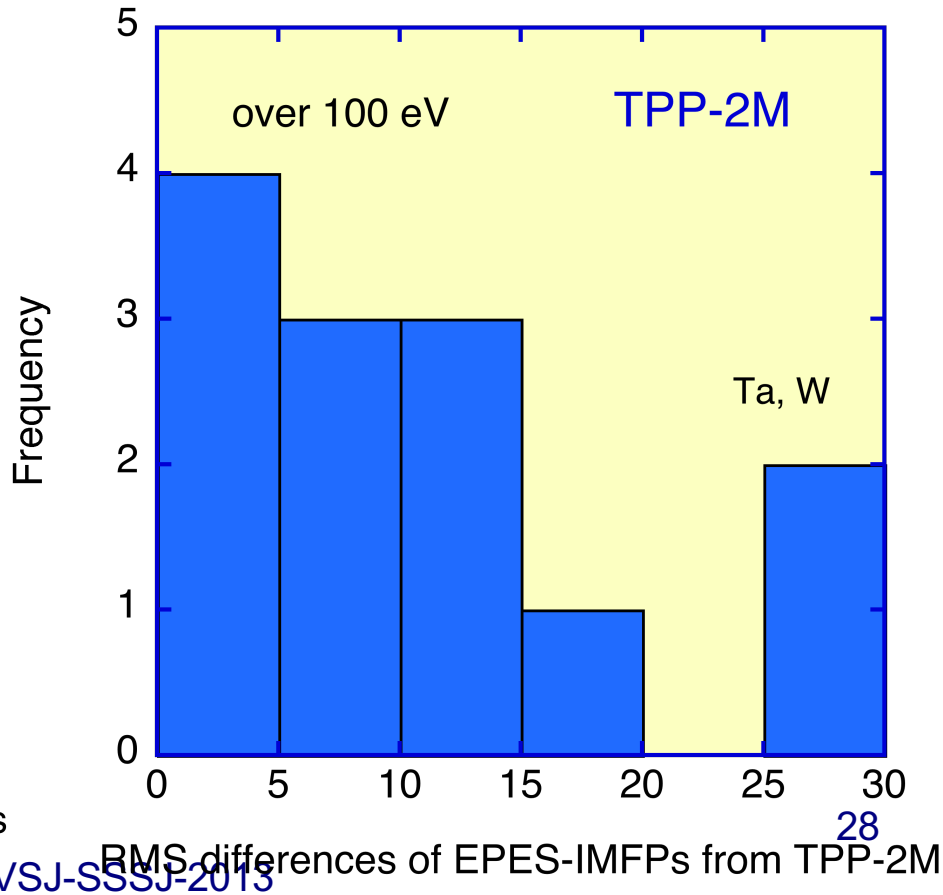




RMS (%) difference of IMFPs
- IMFPs of the Penn algorithm (optical IMFPs) and the TPP-2M

Average RMS(%) in 100 - 5000 eV : 11.0%(optical) : (11 elms.)
10.7%(TPP-2M) : (13 elms.)





Summary : IMFP calculations

- We calculated IMFPs for 41 elemental solids and 30 compound semiconductors from experimental and calculated optical data for electron energies from 10 eV to 200 keV using relativistic FPA

- Relativistic Modified Bethe equation fits optical IMFPs well over 50 eV – 200 keV. Average RMS : 0.8% for elemental solids, 0.7% for semiconductors.

- **Relativistic TPP-2M equation provides reasonable estimates of IMFPs over 50 eV – 200 keV.**
  Average RMS : < 12% in both group.
  : down to < 9%
  (except for graphite, diamond, Cs and BN)

Summary -2

- We also carried out the experimental determinations of IMFPs for 13 elemental solids in the 50-5000 eV energy range from backscattered EPIs using a Ni reference together with MC.

- The IMFPs determined from EPES could be fit by a simple Bethe formula in the 100 – 5000 eV energy range using Fano plot (average RMS deviation : 9%)

- **The EPES-IMFPs of Ag, Au, Cr, Cu, Fe, Pt, Si, Ta and W are in excellent agreement (RMS deviations is less than 11%) with those calculated from the Penn algorithm (optical IMFPs) in the 100-5000 eV energy range.**

4. Applications to surface analysis

- Mean Escape Depth, MED : *D*

- essential quantity for HAXPES

- convenient measure of surface sensitivity (IMFP, EAL)

: ignore elastic scattering → $D = \lambda \cos(\theta)$

: include elastic scattering (ISO definition) →

$$D = \frac{\int_0^\infty z\phi(z,\theta)dz}{\int_0^\infty \phi(z,\theta)dz}$$

: no simple MED eq. (HAXPES with linearly polarized X-ray)

- calculate wide energy range of MEDs for Si, Cu, Au

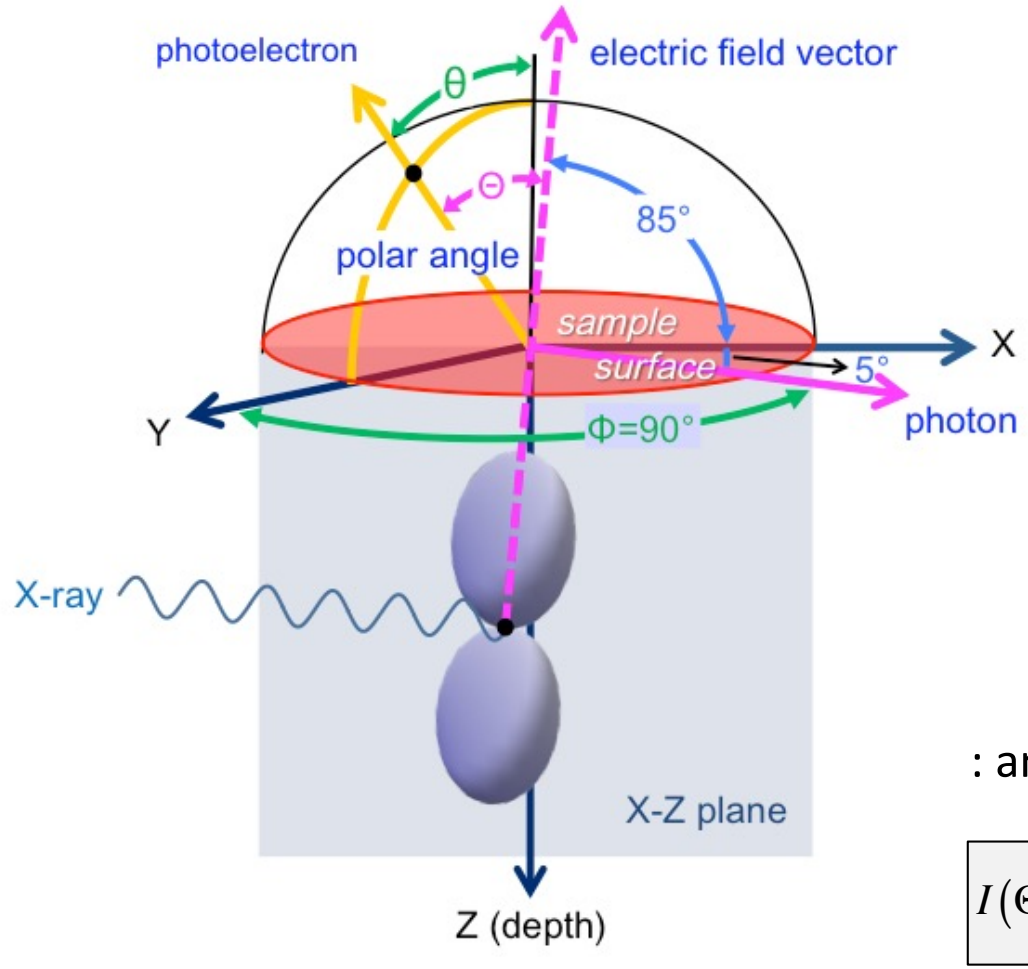
: 50 eV – 10 keV of PEs excited by linearly polarized X-ray

: dependence on **photoelectron energy, emission angle**

dipole parameter (asymmetry parameter)

- **simple MED equation for practical high energy XPS analysis**

Calculation of MED



Schematic diagram of the experimental configuration for Monte Carlo calculations

- **X-ray incident angle : 85°**
- **Emission angle : θ = 0° - 80°** (10° st
- **Azimuthal angle: Φ = 90° , 0°**

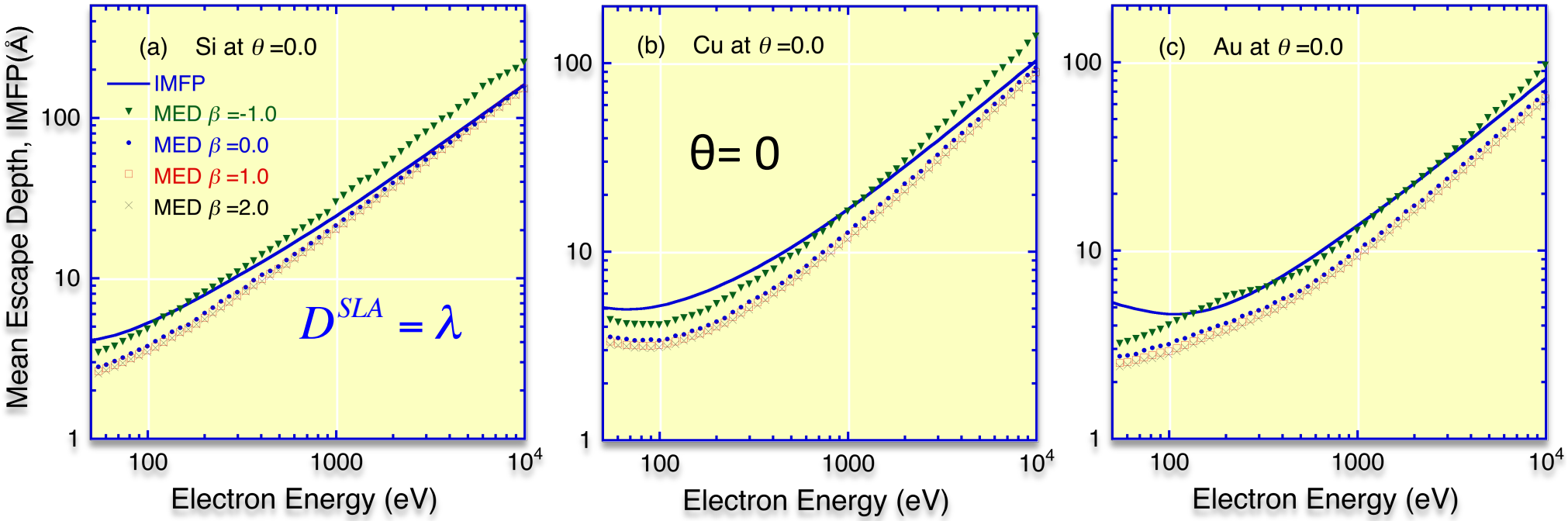
- PE kinetic energy : 50 eV – 10keV
- β = -1 to 2 (0.5 step)
  γ = 0, δ = 0 (multi-pole)

: angular distribution of PEs

$$I(\Theta)=\frac{\sigma}{4\pi}\left[1+\frac{\beta}{2}\left(3\cos^2\Theta-1\right)\right]$$

$$I(\Theta)=\frac{\sigma}{4\pi}\left[1+\frac{\beta}{2}\left(3\cos^2\Theta-1\right)+\left(\gamma\cos^2\Theta+\delta\right)\sin\Theta\cos\Phi\right]$$

Results of Mean escape depth ; *D*

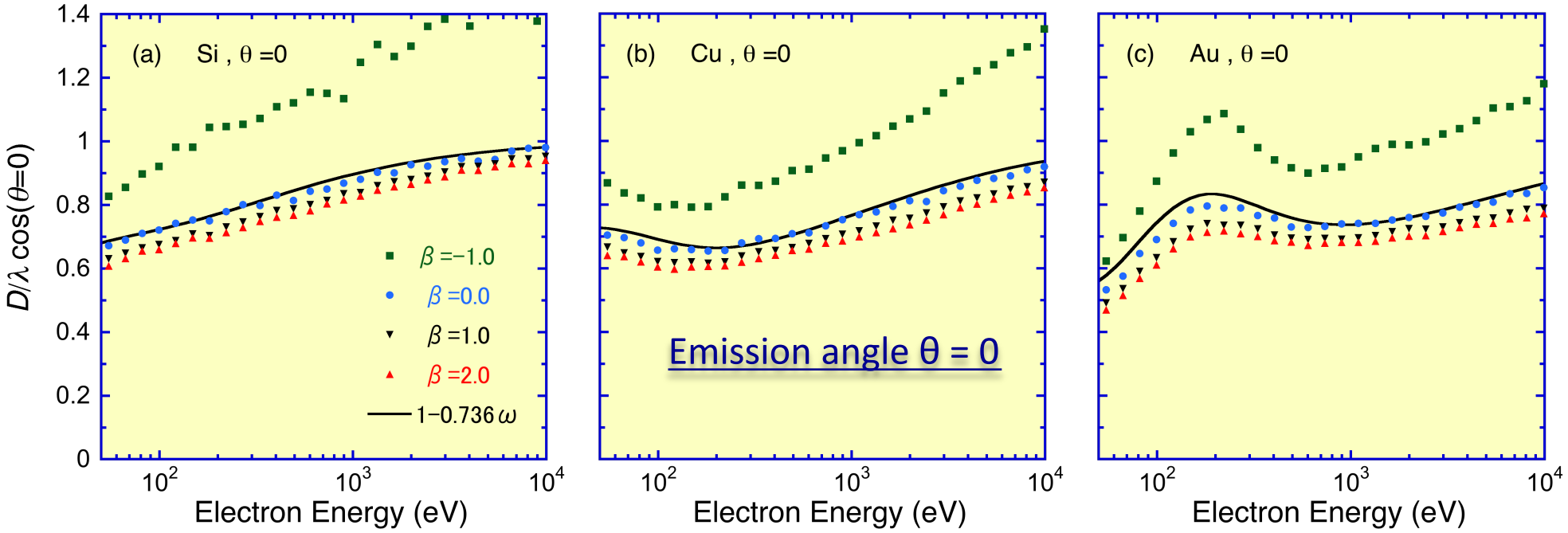


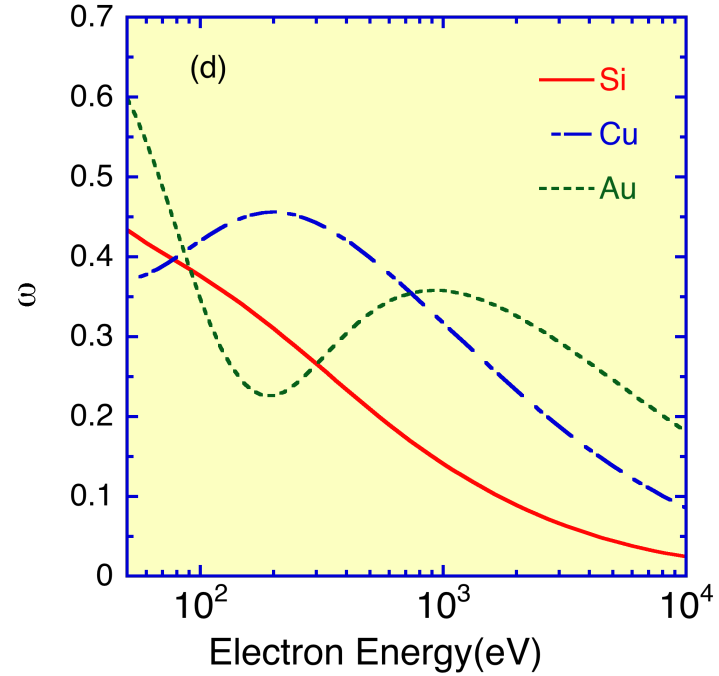
: different energy dependence compared to IMFPs

- MEDs < IMFPs ($0 \leq \beta \leq 2$)
- large deviation at $\beta = -1$

: large elastic scattering effect at low energy region

3. Analysis of MED: **Dependence on Electron Energy**





Jablonski-Powell equation

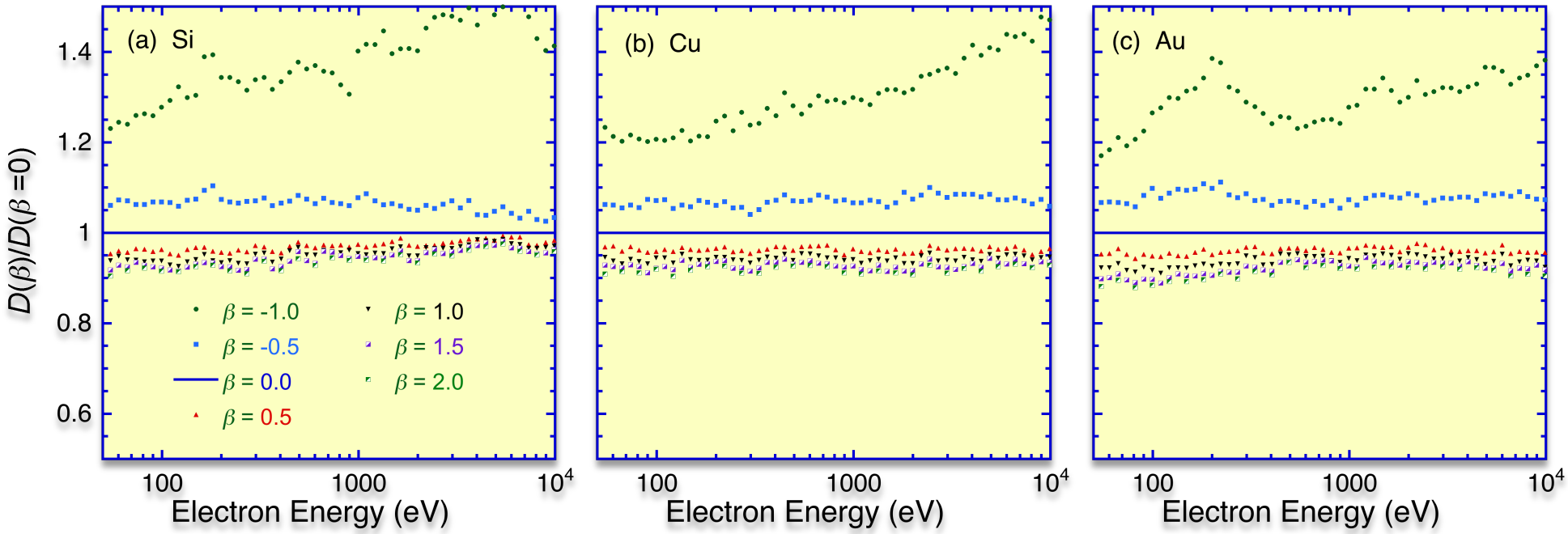
$$\frac{D}{\lambda\cos(\theta=0)} = 1 - 0.736\omega$$

- good guide in wide energy range
- slightly larger than MC results (β ≥ 0)

- no β dependence

3. Analysis of MED: **Effect of asymmetry parameter**

D(β)/D(β=0) vs. Photoelectron energy : Emission angle θ = 0 :



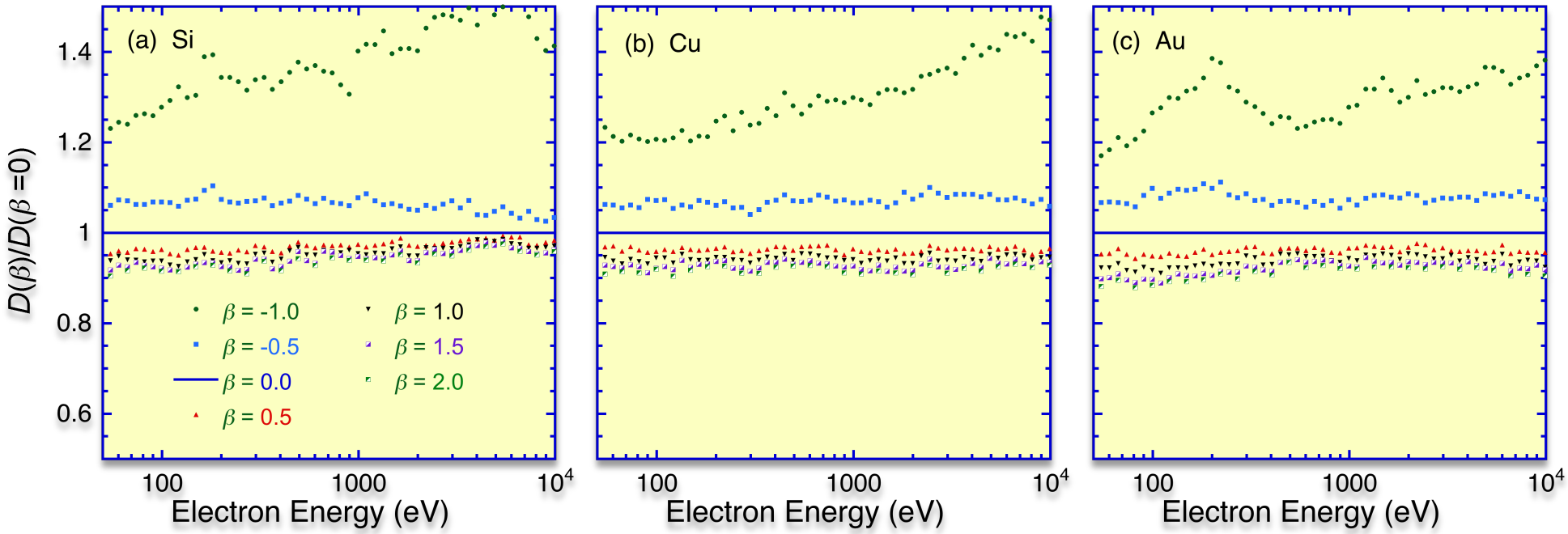
: the ratio *D(β)/D(0)* as a function of PE energy

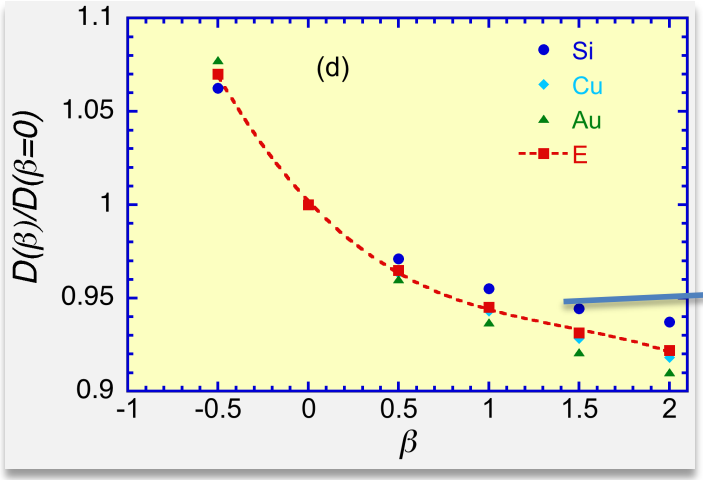
- approximately constant (except $\beta = -1$)
  relative RMSs < 2.1 % ($-0.5 \le \beta \le 2.0$)

- fit the plot of average ratios of D(β)/D(0) with Poly. Eq. of β

3. Analysis of MED: **Effect of asymmetry parameter**

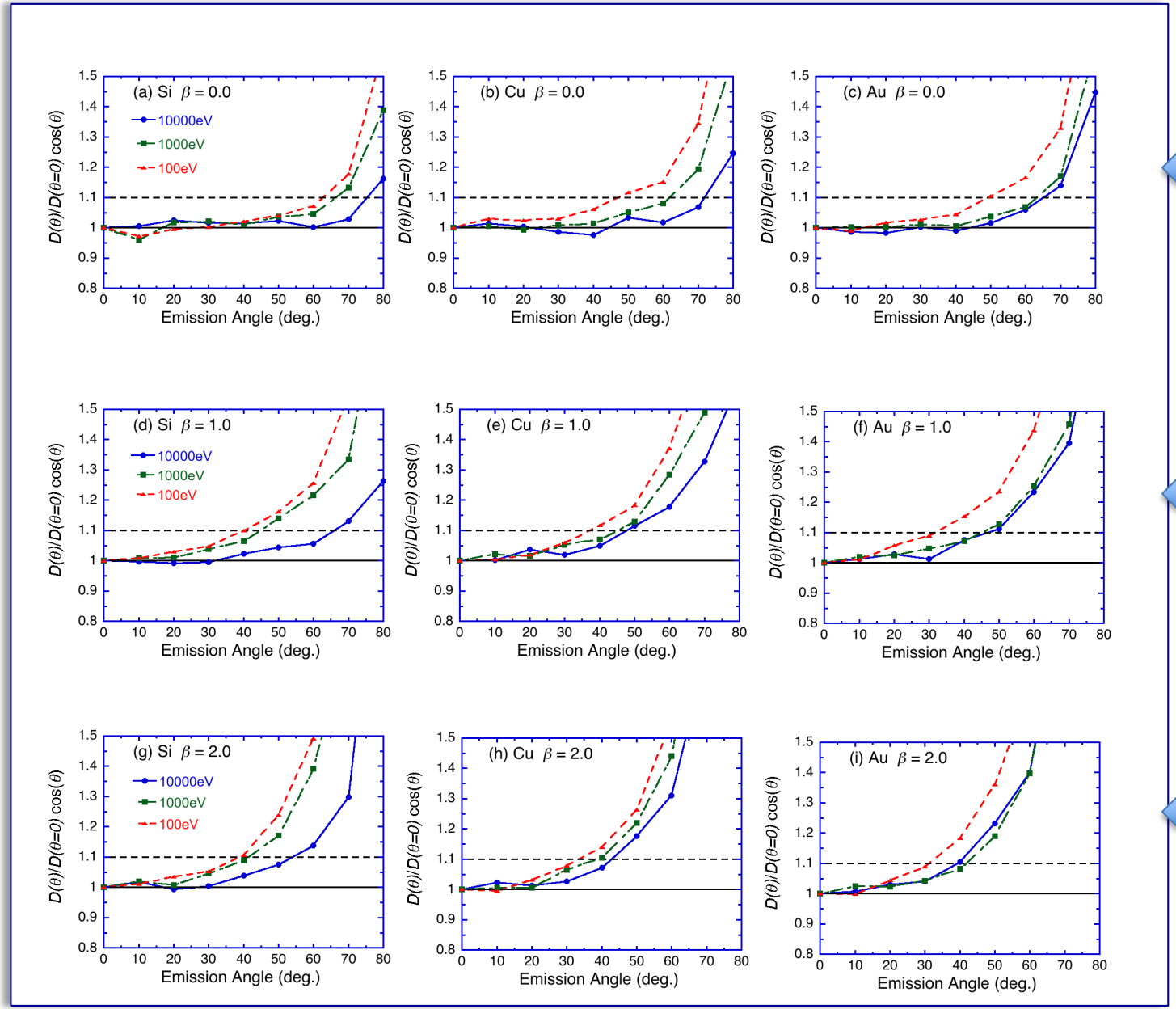
Emission angle θ = 0 : D(β)/D(β=0) vs. Photoelectron enenrgy





$$f(\beta)=\frac{D(\beta)}{D(\beta=0)}=1.00-0.102\beta+0.0577\beta^2-0.0133\beta^3$$

Normalized MED , D(θ)/D(0) cos(θ) vs. emission angle θ



β=0

: ≥1000 eV
θ≤60°
:100 eV
θ≤50°

β=1

: ≥1000 eV
θ≤45°
:100 eV
θ≤30°

β=2

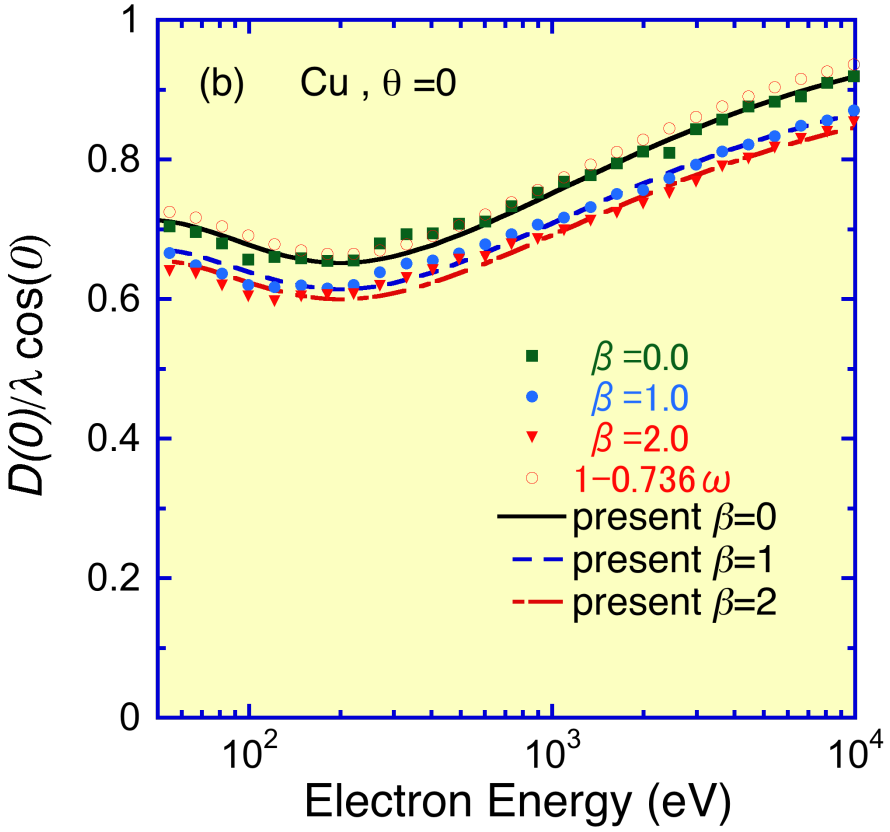
: ≥1000 eV
θ≤40°
:100 eV
θ≤30°

Resulting MED equation for Linearly Polarized X-ray

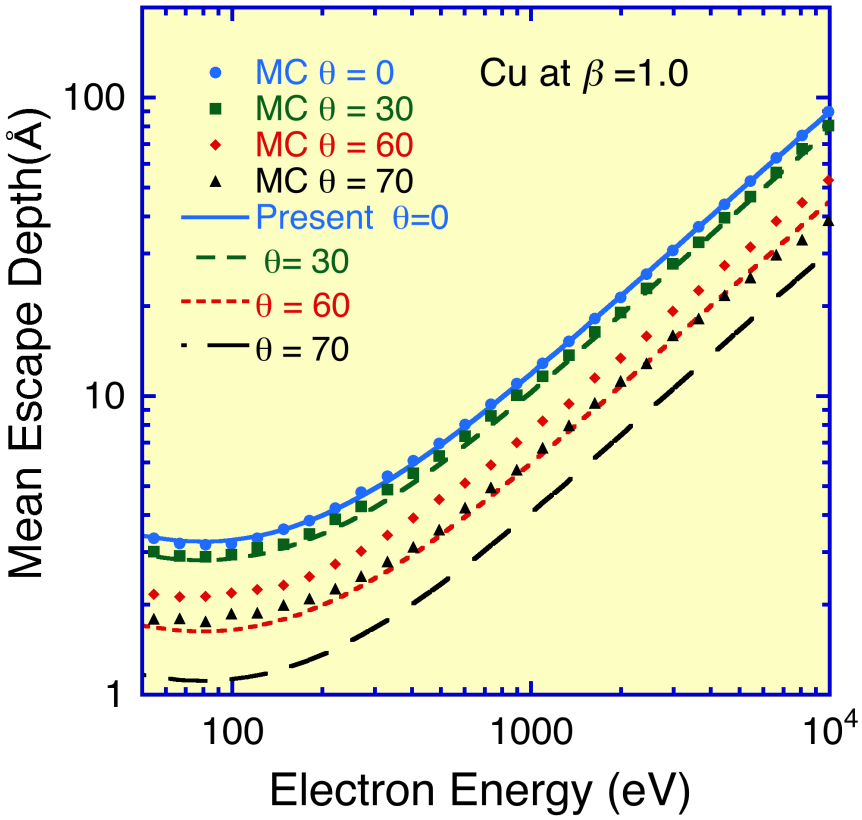
$$D(E,\theta,\beta,\lambda,\omega) = g(\beta)\times 0.981(1-0.736\omega)\lambda\cos\theta$$

$$g(\beta) = 1.00 - 0.102\beta + 0.0577\beta^2 - 0.0133\beta^3$$

Energy range : 100 eV – 10 000 eV
Emission angle : 0° ≤ θ ≤ 40°
Asymmetry parameter: -0.5 ≤ β ≤ 2.0



- MED on β dependence at θ=0



- MED on θ dependence at β=1

Summary

- MEDs of PEs excited by linearly polarized X-rays in Si, Cu, and Au over the 50 to 10,000 eV. (MC method)
- MED values increase as the β values decrease over the 50 to 10,000 eV .
- Energy dependences of the ratios $D/\lambda\cos(\theta)$ *at* $\theta=0$ can be expressed by the form of Jablonski-Powell predictive equation , which is a function of single-scattering albedo, over 50 eV to 10,000 eV.
- $D(\theta)/D(0)\cos\theta$ are approximately constant to within 10% for
  - $0^\circ \le \theta \le 40^\circ$, $-0.5 \le \beta \le 2.0$, and $E \ge 1000$ eV

  ($0^\circ \le \theta \le 60^\circ$, $\beta = 0$, and $E \ge 1000$ eV)

: a simple predictive MED equation that could be applied to the wide energy range and dipole parameter that are used in high-energy XPS with synchrotron radiation.

These works were performed in collaboration with

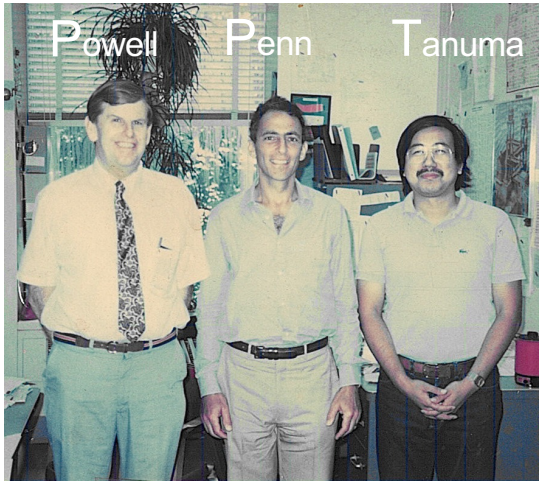
C. J. Powell, D. R. Penn (NIST) : IMFP calculations

H. Yoshikawa (NIMS) : REELS- FA, MED

K. Goto (NIT, AIST) : EPI measurements

R. Ueda (NIMS) : MED

H. Shinotsuka (NIMS, AA&S) : OCs and programing



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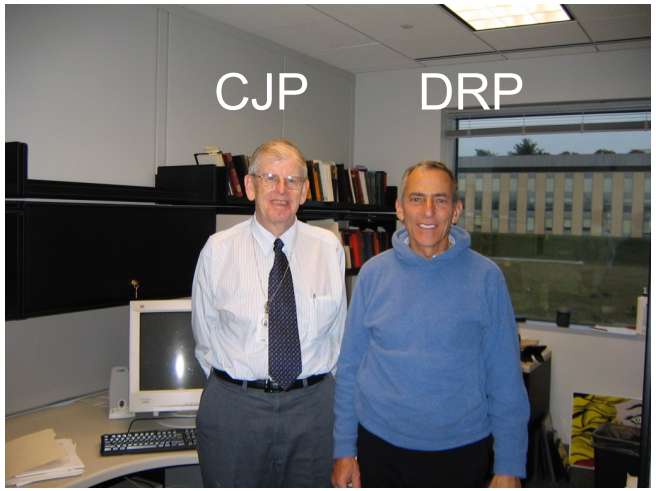

Nov. 2004

Jun. 2013

Thank you for your attention !