Interdisciplinary Study with Quantum Beams

- Application to materials analysis

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1. Materials analysis：what do we want to know?
2. Quantum beams
   - e^-, e^+, Photon, Ion, Neutron, Muon
   - Interaction of the beams with materials
   - Information obtained by the beams
3. Application: H in Pd
   - Energetics, dynamics, and kinetics
   - Quantum effects and chemical reaction
4. Summary

Development of novel materials

Materials properties

Electrical

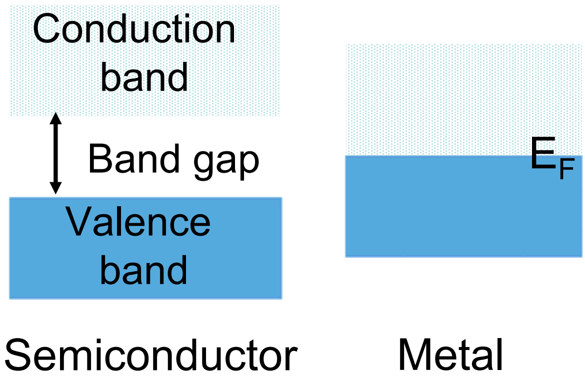
Magnetic

Optical

Chemical

. . . . .

Electronic band structure



✓ What we want to know:

Structure and element composition

atomic, mesoscopic, macroscopic scales

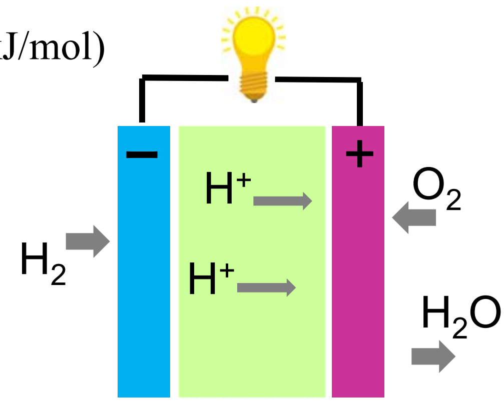
→ prediction, design, and production of highly functional materials

Energy-related materials: battery

- Fuel cell $H_2 + \frac{1}{2}O_2 \rightarrow H_2O + Q(286\,\mathrm{kJ/mol})$

  Reaction at electrode surfaces

  Proton transport

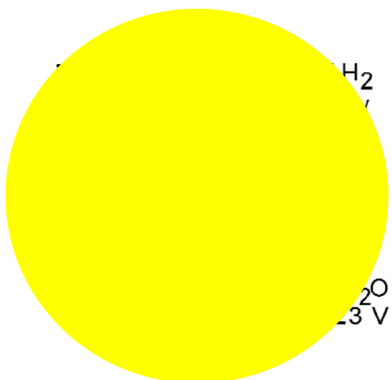


Cf. Photocatalytic H_2 production

H storage in materials

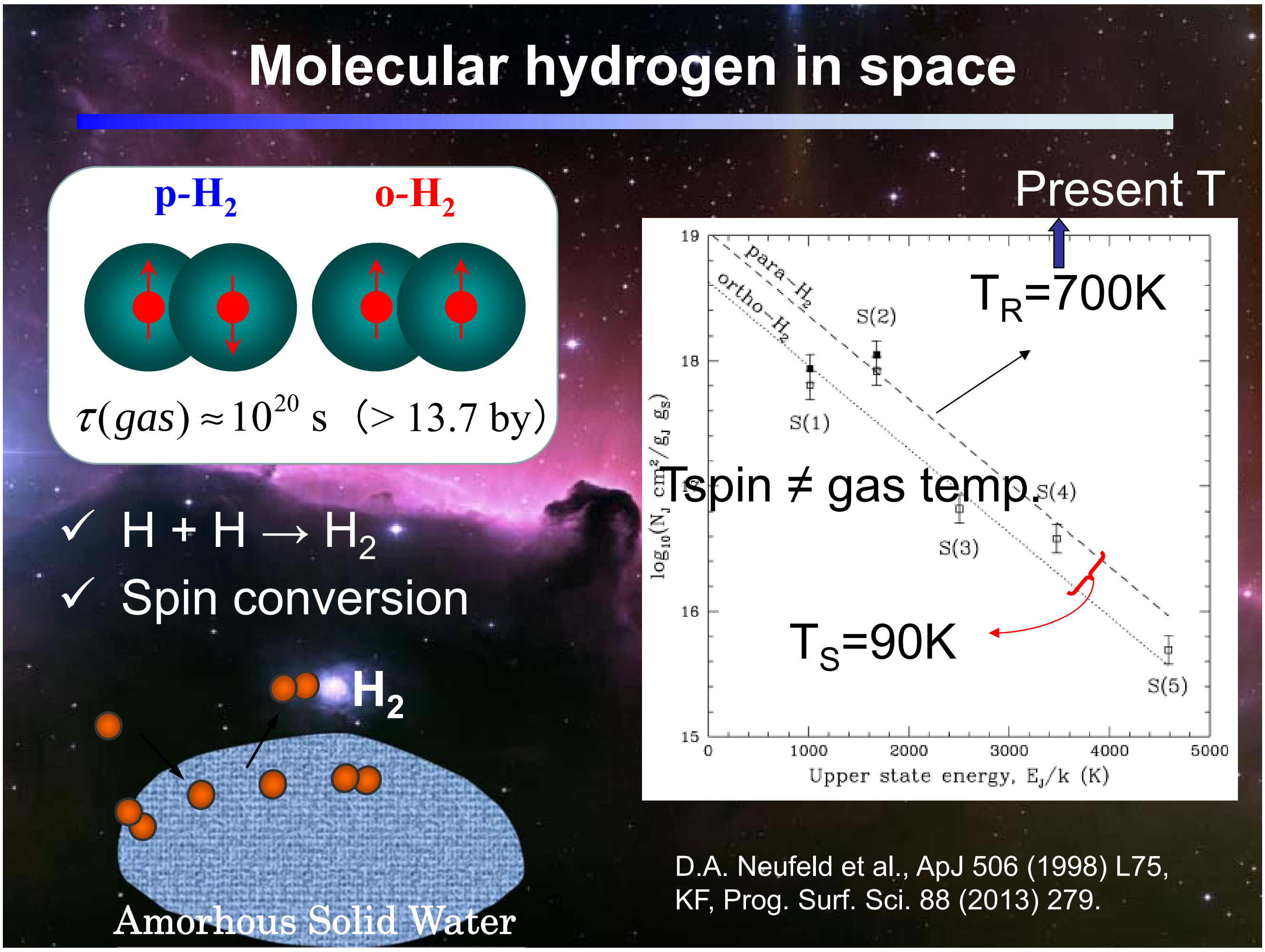
- Li-ion battery

  Li ion transport → electricity



➡ Surfaces & interfaces are important

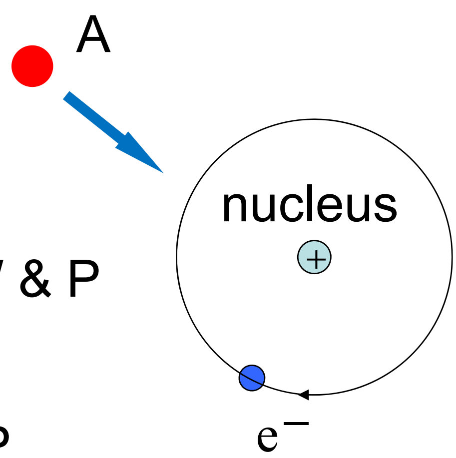
Light elements often play key roles



Quantum beam

Interaction with materials (aggregates of atoms)

A	Interaction	
e^-, e^+ :	Coulomb force	W & P
Photon :	Charge density	W & P
Neutron:	Nuclear force	W & P
Ion:	Coulomb+Nuclear	P



Wave/ particle duality

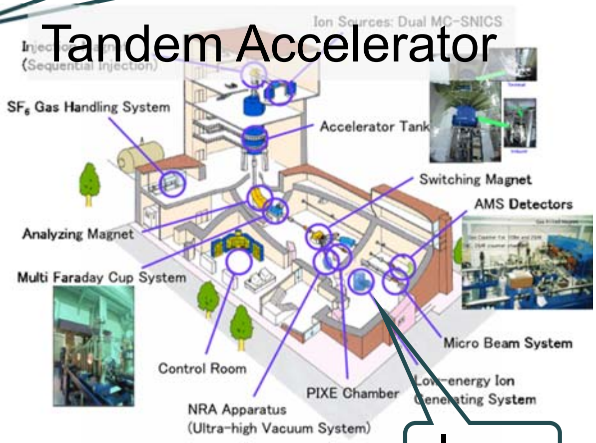
$$\lambda = \frac{h}{p}$$

Quantum beam facilities in Japan

23 Neutron beam lines

3 Muon beam lines

Tandem Accelerator



Ions

KEK: PF

UV – X ray, e^+

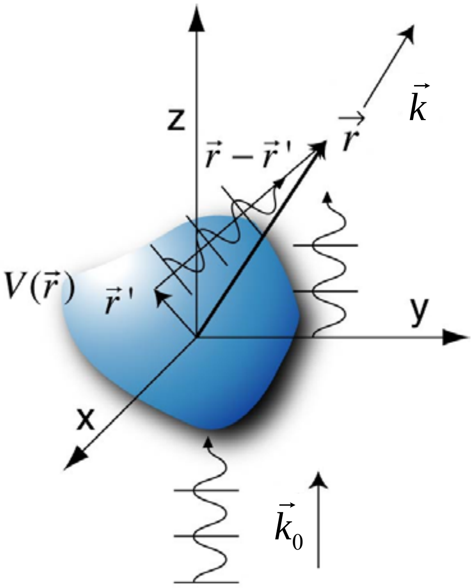
Spring-8

Elastic scattering of wave

$$\left[-\frac{\hbar^2}{2m}\Delta + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r})$$

$$\frac{2m}{\hbar^2}V(\vec{r}) = U(\vec{r}), \quad E = \frac{\hbar^2}{2m}k^2$$

$$\left[\Delta + k^2\right]\psi(\vec{r}) = U(\vec{r})\psi(\vec{r})$$



$\exp(i\vec{k}_0\cdot\vec{r})$

Solution in the integral form

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int G(\vec{r},\vec{r}')U(\vec{r}')\psi(\vec{r}')d\vec{r}$$

Incident wave

Scattering wave

Cf.) Green function for a free particle

$$G(\vec{r},\vec{r}') = -\frac{1}{4\pi}\frac{\exp(ik|\vec{r}-\vec{r}'|)}{|\vec{r}-\vec{r}'|} \qquad \left[\Delta + k^2\right]G(\vec{r},\vec{r}') = \delta(\vec{r}-\vec{r}')$$

Elastic scattering of wave: diffraction

Weak scattering (Born approx.)

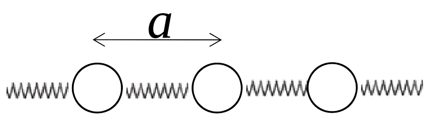
$$\psi^S(\vec{r}) \approx \frac{\exp(ikr)}{4\pi r}\int \exp(i(\vec{k}_0-\vec{k})\cdot\vec{r}')U(\vec{r}')d\vec{r}'$$

Spherical wave

Scatt. Amplitude (in the k direction)

= Fourier transform of potential

Crystal: periodic potential

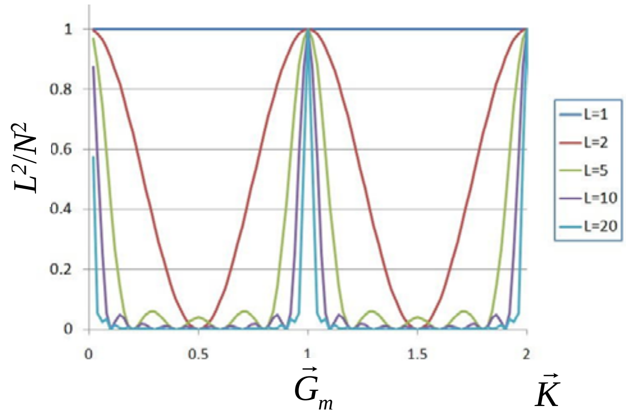


$$U(\vec{r}) = \sum_{\vec{R}_n} U_{unit}(\vec{r}-\vec{R}_n)$$

$$\vec{R}_n = n_1\vec{a}_1$$

$$I(\vec{K}) \propto \delta(\vec{K}-\vec{G}_m)$$

$$\vec{G}_m = \frac{2\pi m}{a}$$ Reciprocal vector



Diffraction→ atomic structure

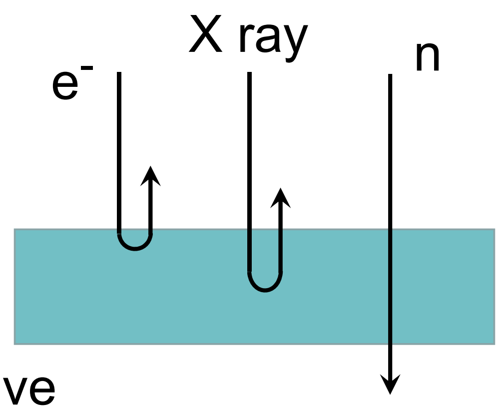
Cross-section

	E (eV)	λ (Å)	σ (cm^2)	Z dep	
e^-, e^+	~100	1.22	~10^{-16}	$\propto Z^2$	Coulomb
Photon	~10^3	1.24	~10^{-21}	$\propto Z^2$	Charge density
Neutron	~0.1	0.90	~10^{-24}	-	Nuclear
Ion	~10^6	~10^{-4}			

✓ λ ~ Interatomic distance

✓ Penetration length

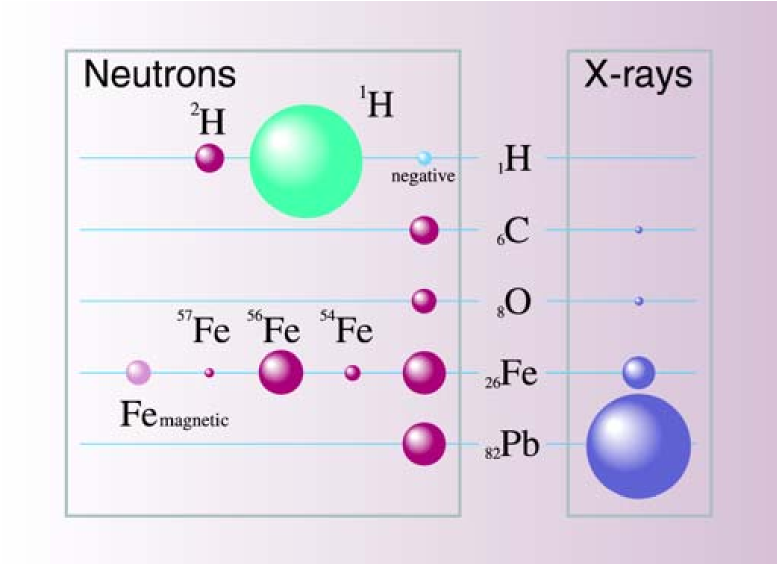
=probing depth



e^-: surface-sensitive

Element specificity

Cross section (~ atomic size)



$\propto Z^2$

Sensitive to heavy atom

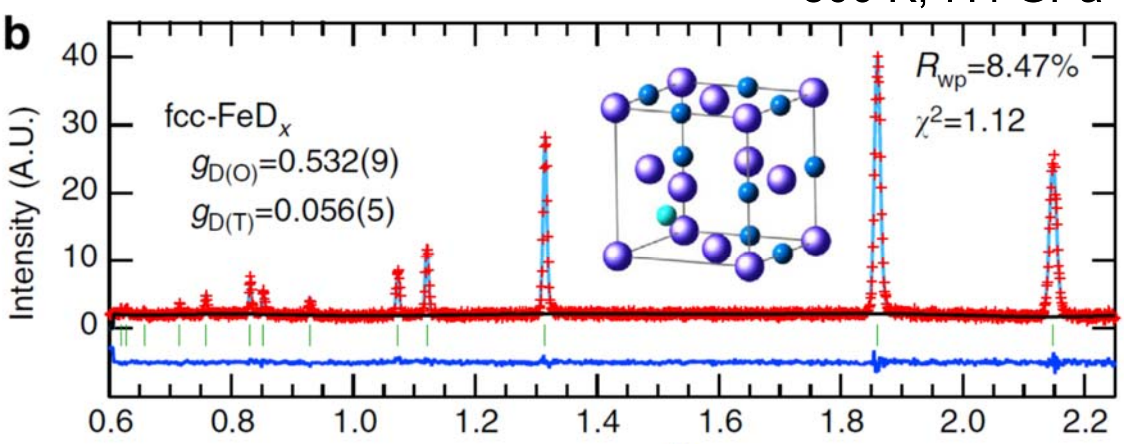
Independent of Z

→ suitable for observation of light atoms

Neutron diffraction

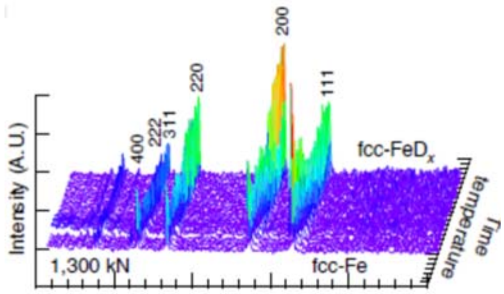
Structure analysis of FeD_x

800 K, 7.4 GPa



Scattering angle → d spacing (Å)

Time evolution: operando



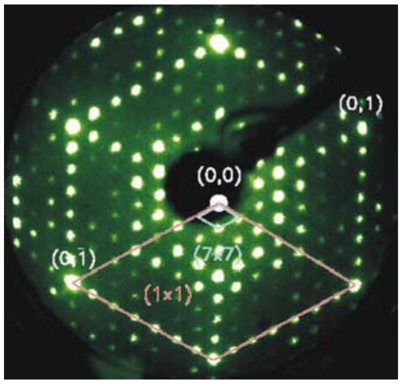
A. Machida et al., Nat. Comm. 5, 5063 (2014)

Electron diffraction

Surface structure

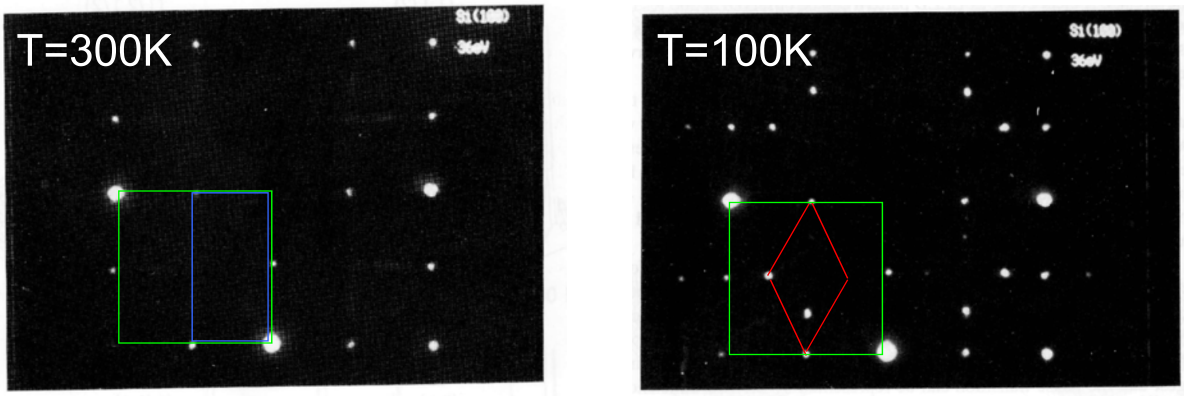
different from the bulk

Si(111)7x7



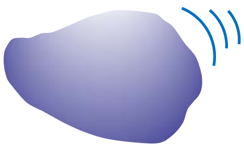
Phase transition

Si(001)



Phys. Rev. B 49(1994)4810.

Inelastic Scattering

A (E=E_0) →  → A (E=E_0 − ΔE)

Energy loss

Photon

Raman scatt.

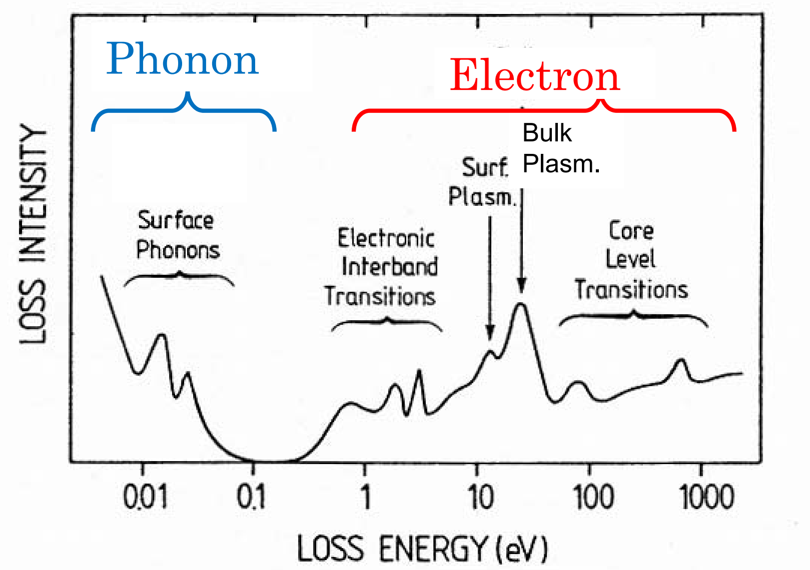
Compton scatt.

Photoemission

e^-, n

Electronic & phonon structures

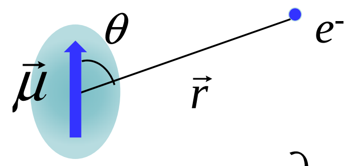
Energy scale



Electron Inelastic scattering due to phonon

Electron-dipole interaction

$$V \cong \frac{\partial}{\partial \vec{r}}\left(\frac{e}{4\pi\varepsilon_0 r}\right)\cdot\vec{\mu} = \frac{e}{4\pi\varepsilon_0}\frac{\vec{\mu}\cdot\vec{r}}{r^3}$$



$$\vec{E} = \frac{\partial}{\partial \vec{r}}\left(\frac{e}{4\pi\varepsilon_0 r}\right)$$

Matrix element of V

$$\langle \psi_f | V | \psi_i \rangle \propto \langle \phi_v^{\,f}(R) | \hat{\mu}(R) | \phi_v^{\,i}(R) \rangle$$

$\vec{R}$: atom position

$$\hat{\mu}(R) = \hat{\mu}_0 + \frac{d\hat{\mu}}{dR}R + \quad \text{Taylor expansion}$$

$$\frac{d\hat{\mu}}{dR}\langle \varphi_v^{\,f}(R) | R | \varphi_v^{\,i}(R) \rangle \Rightarrow \Delta v = \pm 1$$

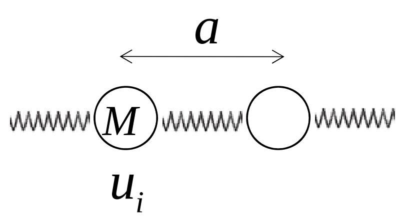
(harmonic potential)

dynamic dipole

Cf. point charge approx. $\hat{\mu}(R) = qR$

Phonon: One-dimensional chain

$$V = \frac{1}{2}\sum_{i=-\infty}^{\infty} k(u_{i-1} - u_i)^2$$



$$M\ddot{u}_i = k(u_{i-1} - u_i) - k(u_i - u_{i+1})$$

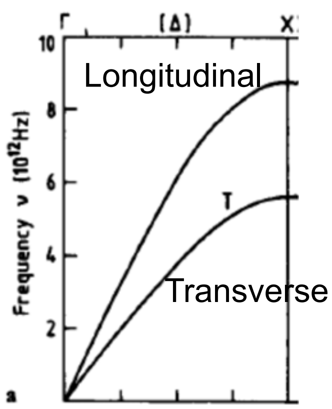
In the form of $u_i = u_i^0 \exp(i\omega t)$

$$\omega^2 M u_i^0 = k(u_{i-1}^{\;0} - u_i^{\;0}) - k(u_i^{\;0} - u_{i+1}^{\;0})$$

$u_n^{\;0} = u^0 \exp(iq(na))$ Bloch theorem

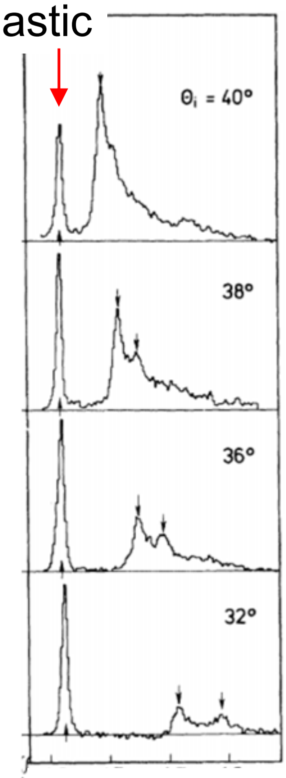
$$-\omega^2 M u^0 = k(\exp(-iqa) - 2 + \exp(iqa))u^0$$

$$\omega = \sqrt{\frac{4k}{M}}\left|\sin\frac{qa}{2}\right|$$



Phonon dispersion: energy vs. momentum

elastic



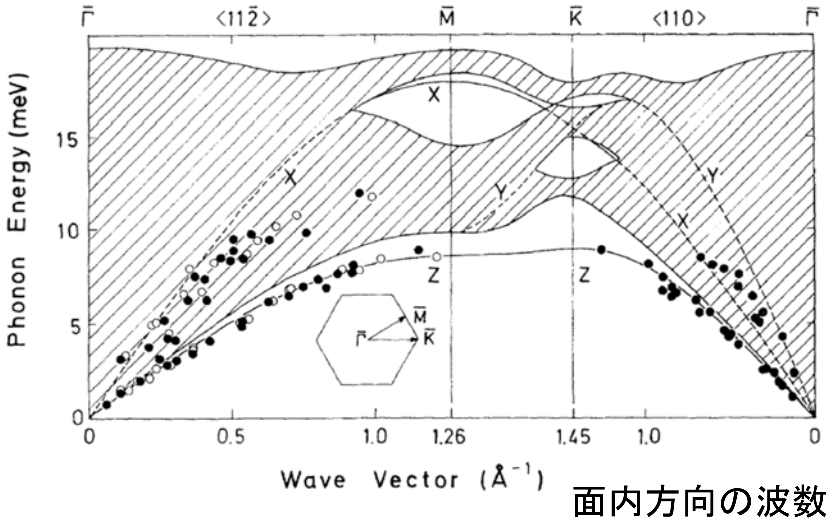
Energy loss

Ag(111)

Scattering angle → momentum

$X:\langle 11\bar{2}\rangle$

$Y:\langle 110\rangle$



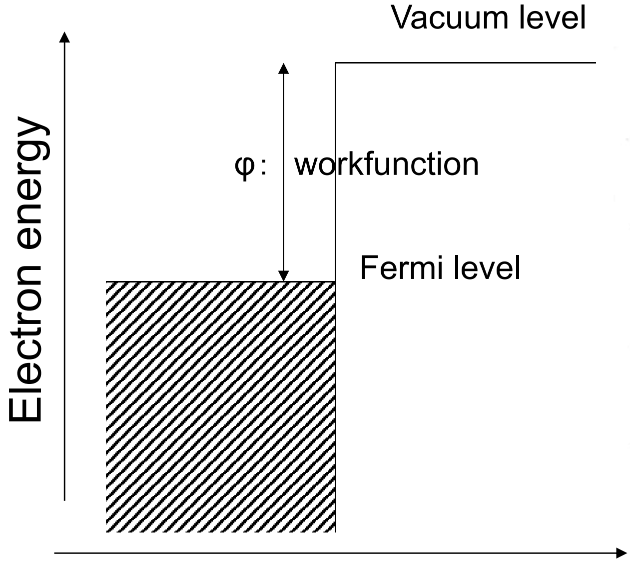
面内方向の波数

PhysRevLett.51.578

Electron emission

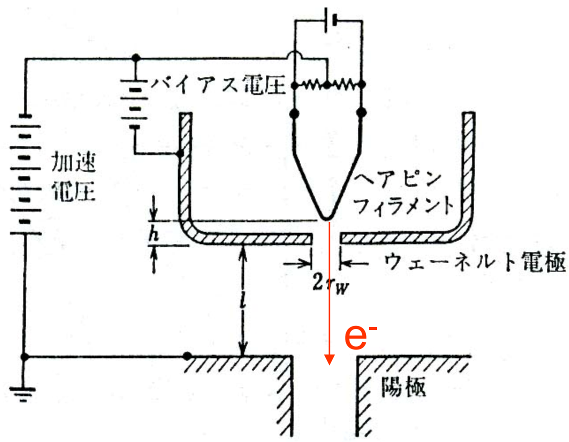
Thermionic electron emission

$$J = A_e T^2 \exp(-\phi / k_B T)$$

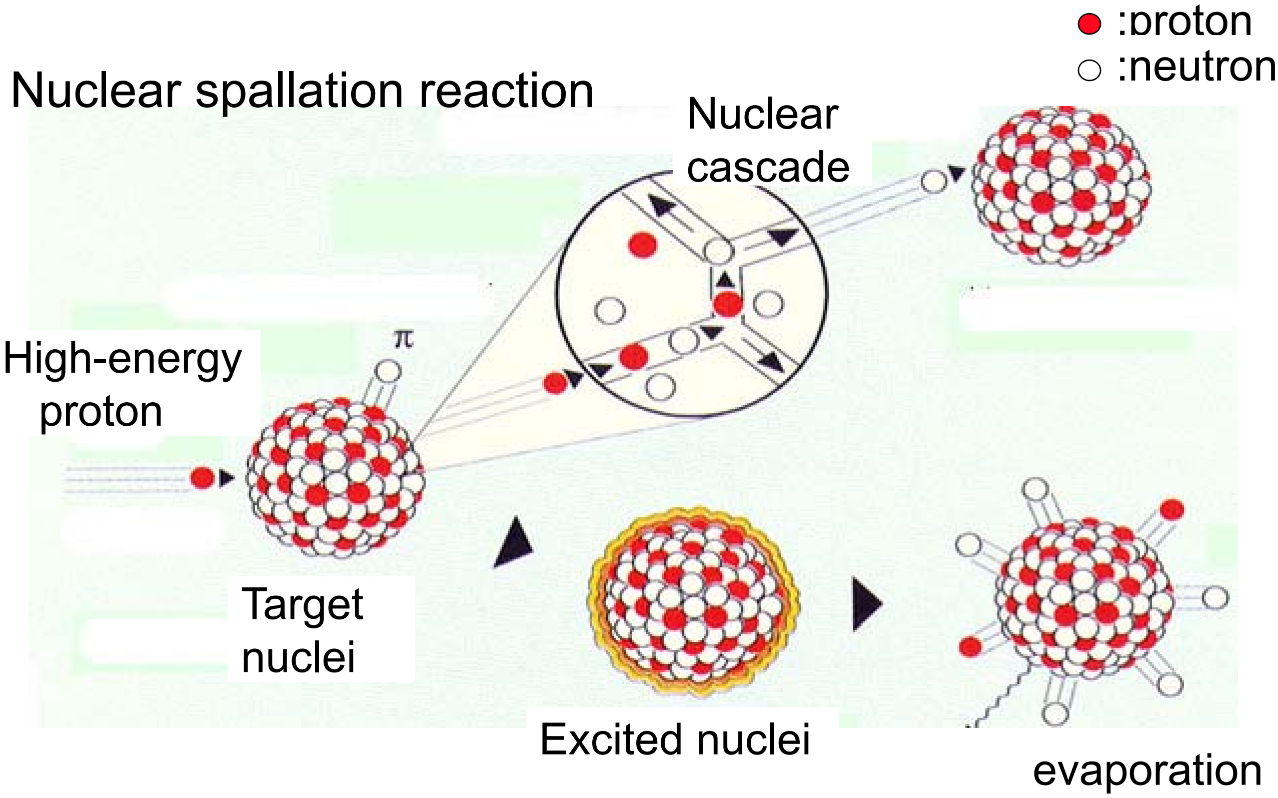


Distance from surface

Electron gun



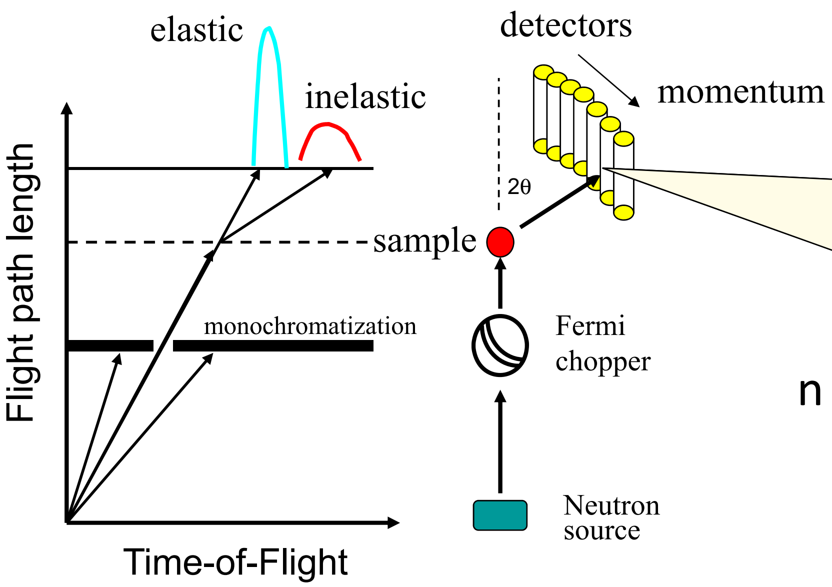
Production of neutron beam

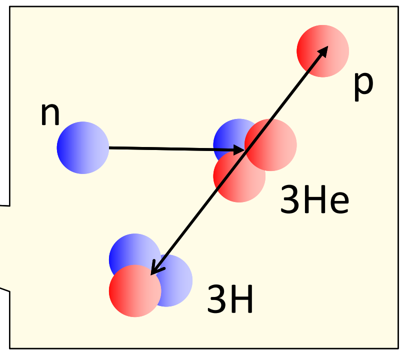


~24n/1GeV proton

Neutron inelastic measurement

- Neutron detector





$n + {}^{3}He \rightarrow$
$p + 3H + 0.765$ MeV

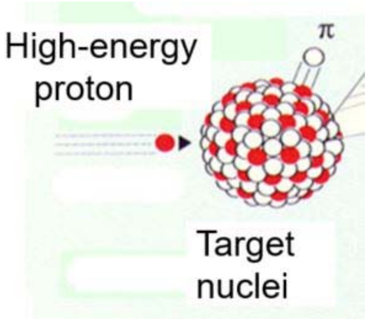
Muon (lepton): μ^+, μ^-

- mass: ~1/9 of proton
- Spin: 1/2
- Gyromagnetic ratio: γ_μ=3.2 γ_p
- Lifetime: 2.2 μs

Magnetic moment

$$\vec{m} = \gamma_\mu \hbar \vec{s}$$

Production of Muon beam



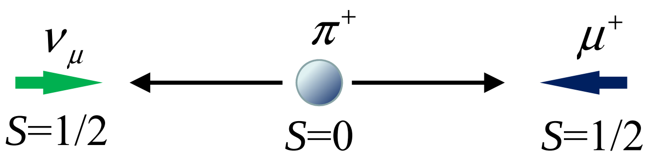
production of π

① μ^+ production

$$\pi^+ \rightarrow \mu^+ + \nu_\mu$$

Spin: antiparallel to velocity

→ μ-spin: polarized

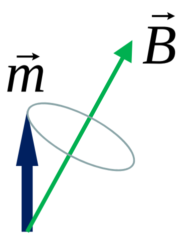


② μ^+ decay

$$\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$$

in the spin direction

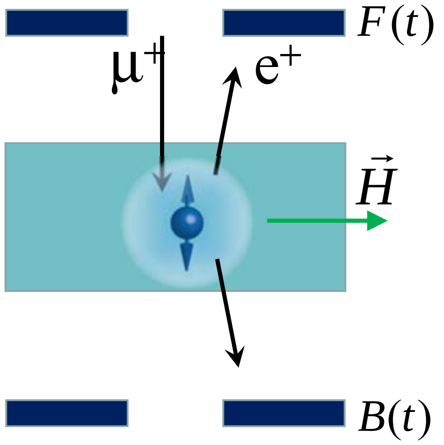
③ Precession under a magnetic field: $\vec{B}$

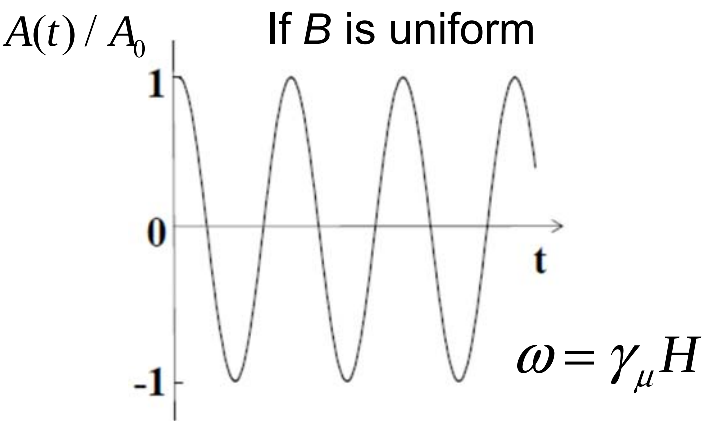


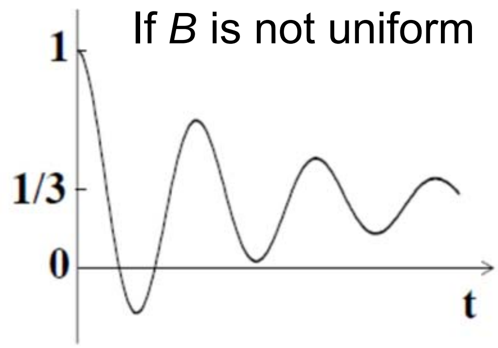
Precession frequency

$$\omega = \gamma_\mu B$$

μ Spin Rotation/ relaxation

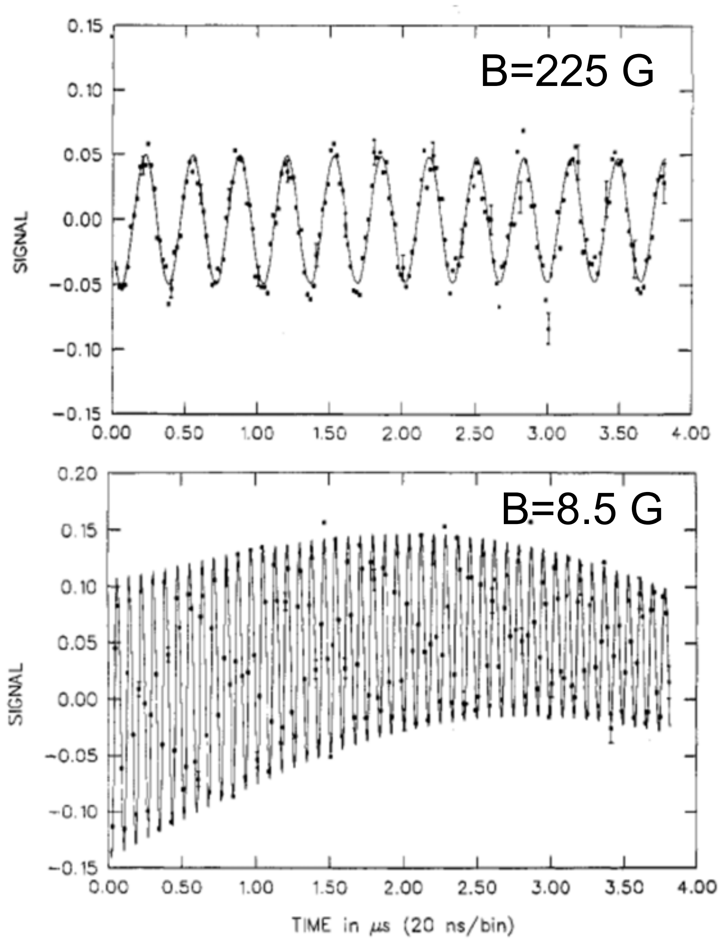






Asymmetry

$$A(t) = \frac{F - B}{F + B}$$



γ~ 8.5x10^4 rad/s/G

➡ μ^+

Much faster oscillation

γ~ 8.7x10^6 rad/s/G

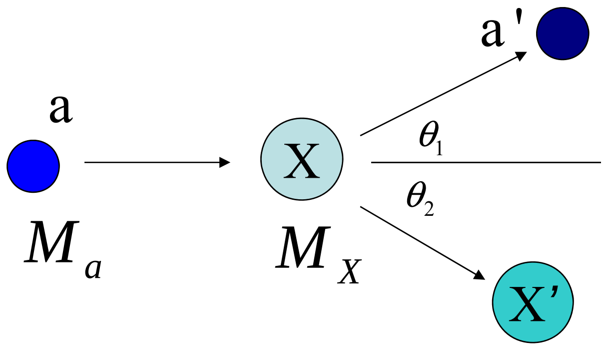
M(μ^+e^-)

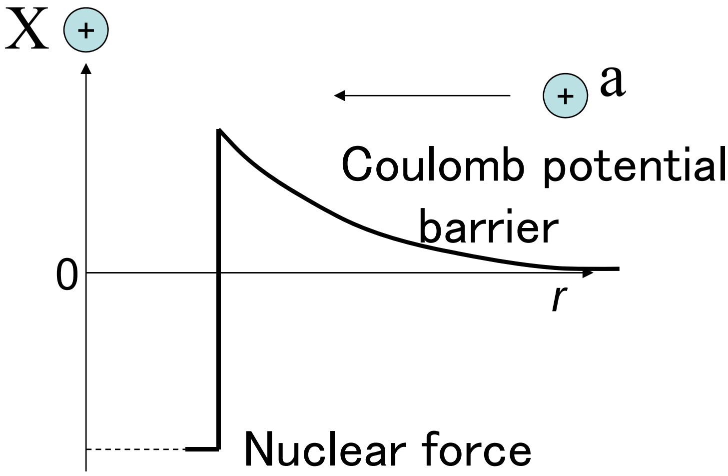
JPC_88_3688 (1984)

Interaction of high-energy ions

Two-body scattering

$$a + X \rightarrow a' + X'$$





E_a : low

a' =a: scattering

E_a : high

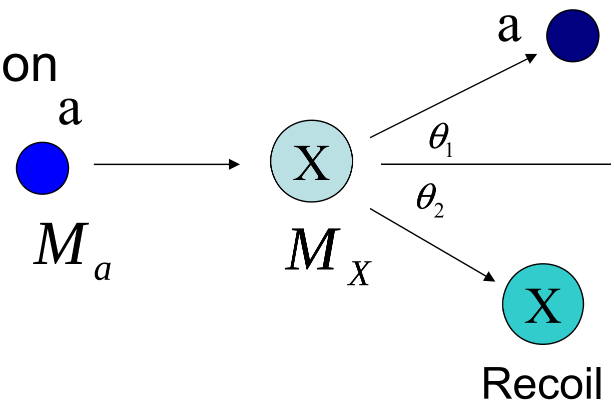
reaction

(light element)

Scattering of high-energy ions

Two-body scattering

via Coulomb interaction



Energy after scattering

$$E' = kE_0$$

(depends on angle & mass)

k-factor: $k \equiv (\frac{v'}{v})^2 = 1 - \frac{4M_a M_X \cos^2\theta_2}{(M_a + M_X)^2}$

Energy analysis→ mass of X =element

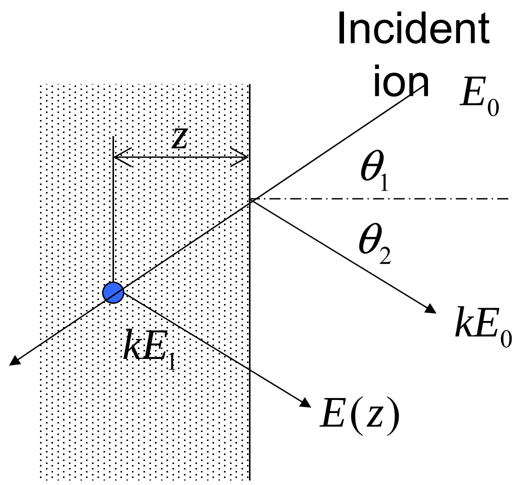
環境（電子状態）に依らない

Energy loss of ions

During passing through a solid

Ions gradually lose energy

Stopping power $S = \frac{dE}{dz}$



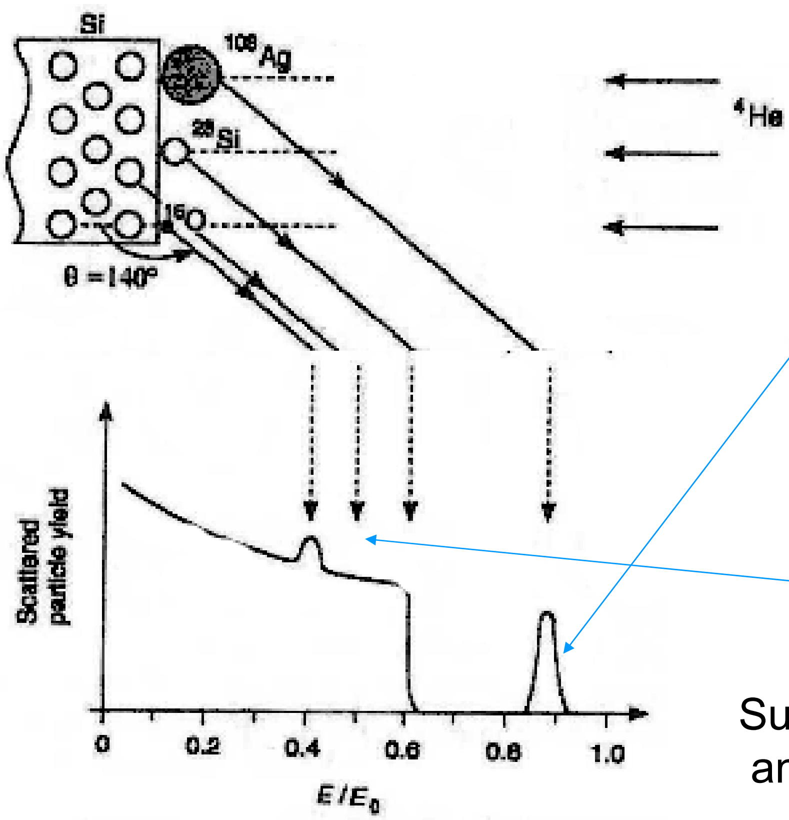
Energy analysis

→ penetration length＝depth

$$E(z) = kE_0 - z\left(\frac{kS_{in}}{\cos\theta_1} + \frac{S_{out}}{\cos\theta_2}\right)$$

Incidence path　　Exit path

Rutherford Back Scattering (RBS)



①Scattering from a heavy element

⇩

Large k-factor → large energy

②Scattering from a deep place

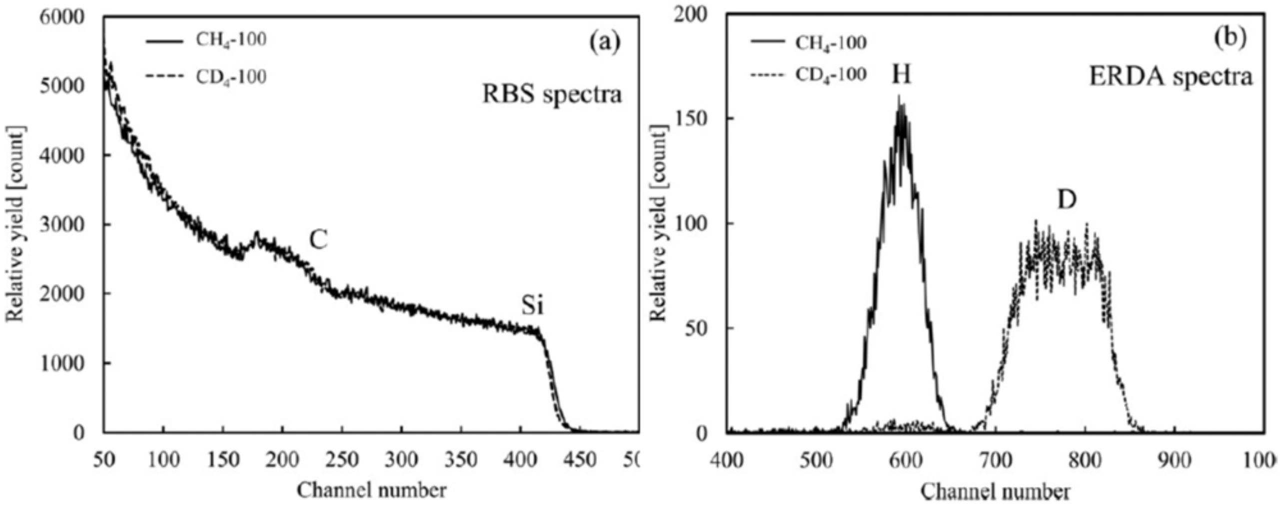
⇩

Low energy

Suited to heavy-element analysis

Elastic Recoil Detection (ERDA)

$CH_4(CD_4)+H_2\,(D_2) \rightarrow$ a-C film/ Si



K. Ozeki *et al,* Appl. Surf. Sci. 265 (2013) 750.

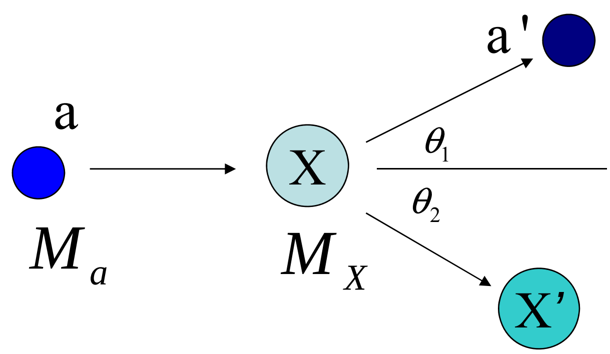
Nuclear Reaction Analysis (NRA)

Nuclear reaction

$$a \neq a', \quad X \neq X'$$

- element-specific
- quantitative

$$a+X \rightarrow a'+X'$$



Coulomb barrier due to nuclei

Suited to light elements

- ✓ Hydrogen
- ✓ Lithium

Recent progress

1. Improvement of resolution & sensitivity

Depth resolution ~ nm

Multi-element analysis: e.g. distinction of N and O

Background reduction: improvement of sensitivity

2. Operando analysis

Materials characterization

under device operation/ reaction

e.g. gas atmosphere, liquid interface

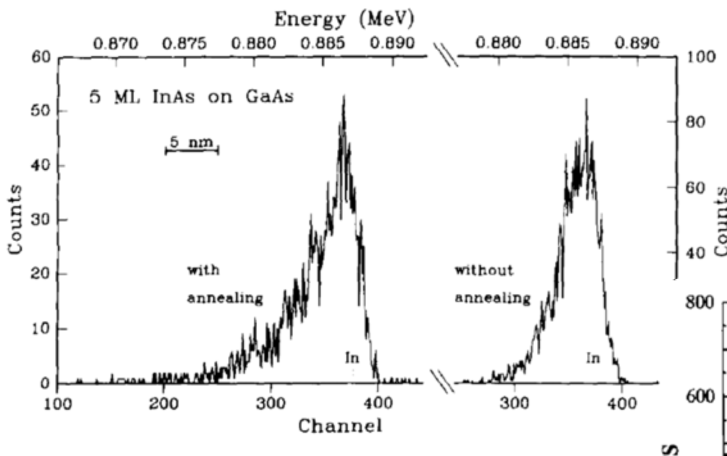
✓ Quantum beams: high penetration in materials

High-resolution RBS

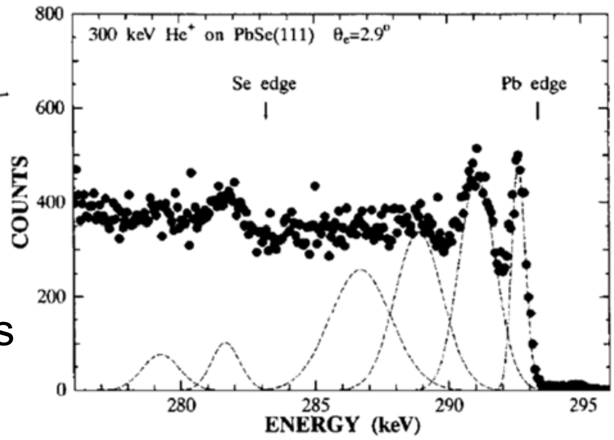
High-resolution energy analysis：nanometer scale analysis

SSD→magnetic analyzer

Depth resolution～1/10



NIMB 64, 817 (1992)



Energy

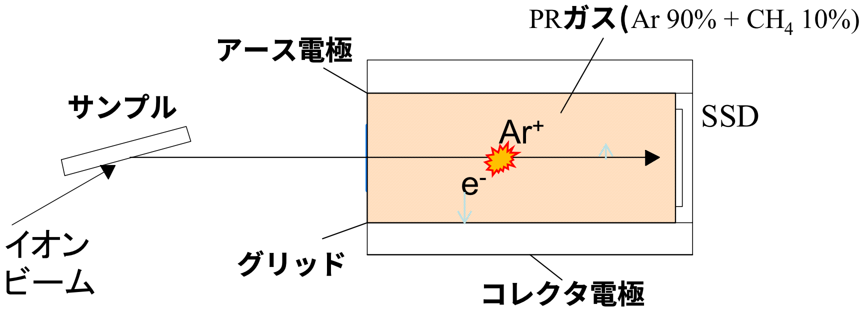
distinction of depth and mass

NIMB 113, 270 (1996)

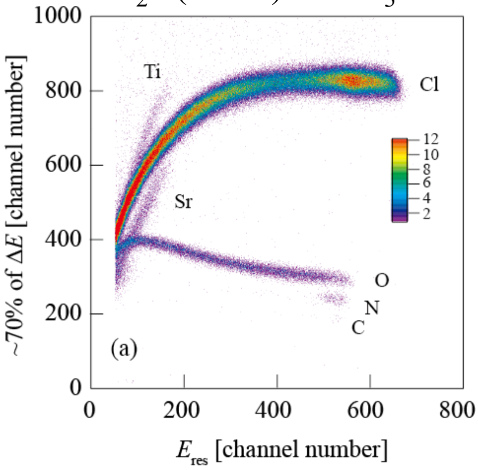
ΔE – E telescope ERDA: depth and mass

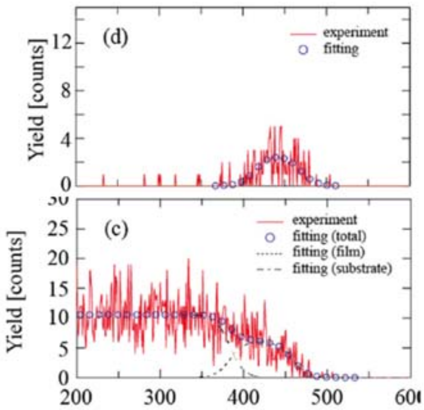
Energy loss in gas

Element identification



$SrTaO_2N$(60nm)/$SrTiO_3$





Nの深さ分布

Oの深さ分布

I. Harayama, D. Sekiba *et al*: NIMB 384 (2016) 61.

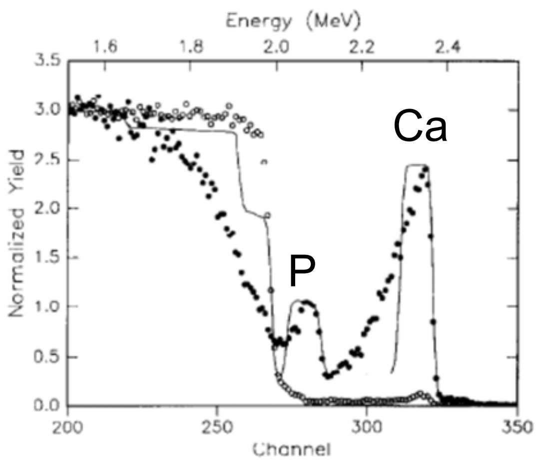
Application to Archeology & Art

Louvre Museum: AGLAE accelerator NIMB 64 (1992) 488.

Usewear characterisation of prehistoric flints with IBA

M. Christensen, Ph. Walter and M. Menu

Laboratoire de Recherche des Musées de France, Palais du Louvre, 75041 Paris Cedex 1, France



Rossendorf, Germany

NIMB 226 (2004) 136.

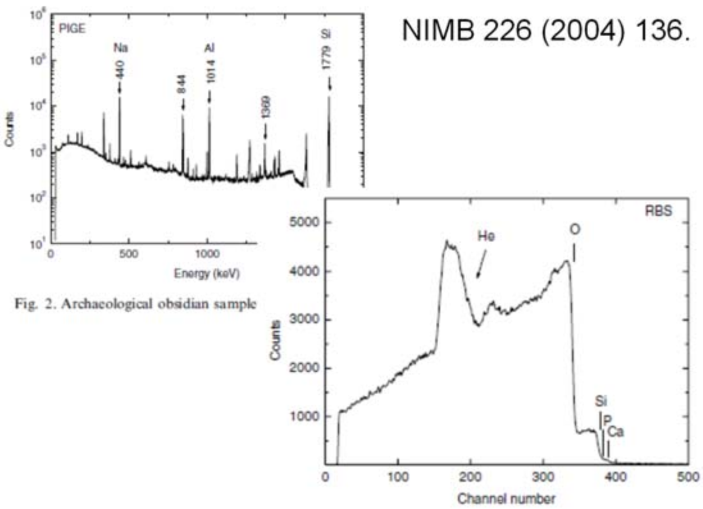


Fig. 2. Archaeological obsidian sample

H detection

$^{1}H(^{15}N,\alpha\gamma)^{12}C$

narrow

width=1.8 keV

D detection

$^{1}D(^{3}He,p)^{4}He$

broad

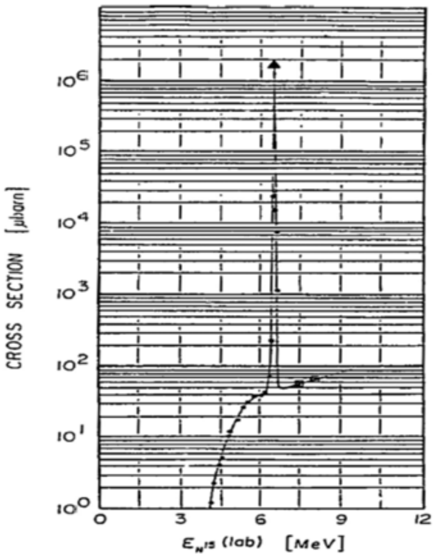
width~500 keV

Li detection

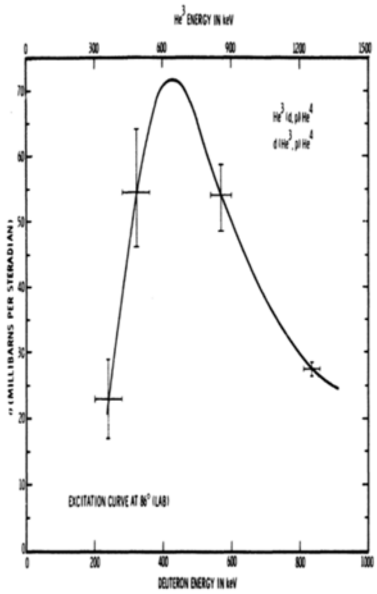
$^{7}Li(p,\alpha)^{4}He$

broad

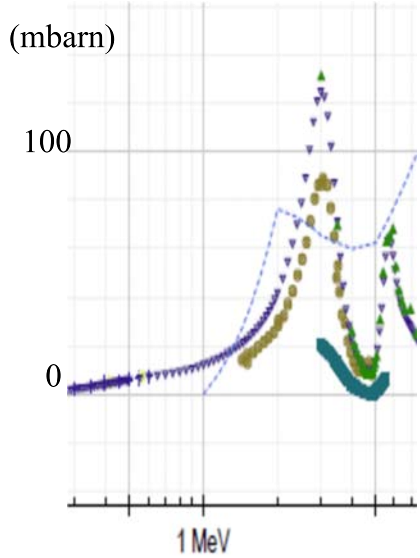
width~1 MeV



NIMB_66_65 (1992)



JNuclMater_53_257 (1974)



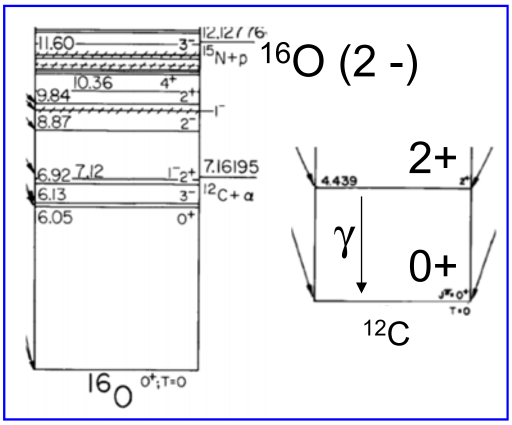
NIMB_66_107 (1992)

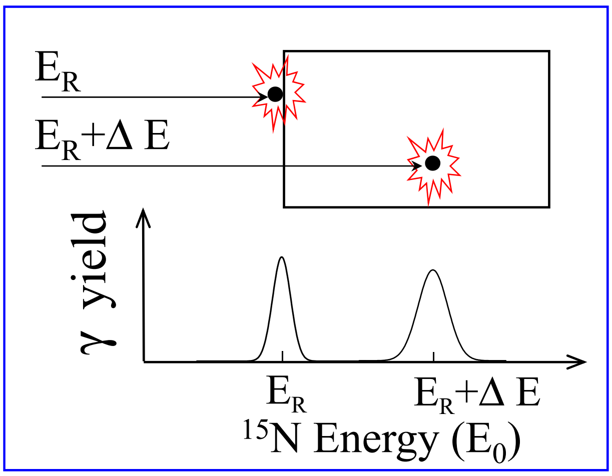
H detection with NRA

$^{15}N+^{1}H \rightarrow ^{12}C+\alpha+\gamma$ (4.43MeV)

Resonance at E_R= 6.385 MeV

width= 1.8 keV





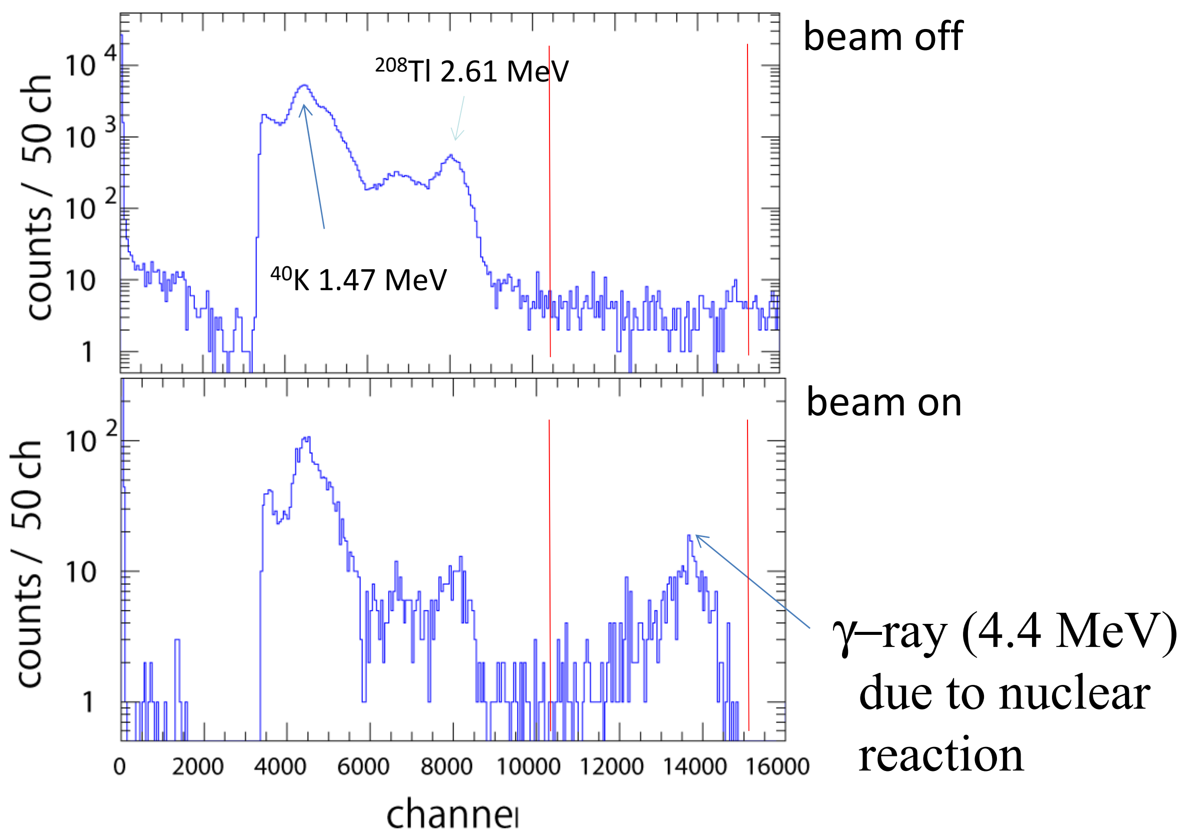
γ–yield vs. ^{15}N energy

H depth profile

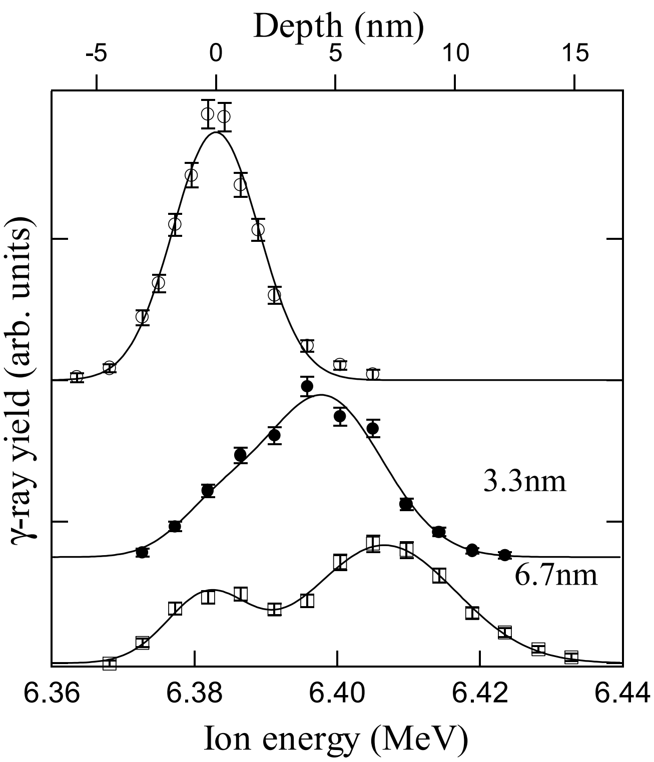
depth resolution

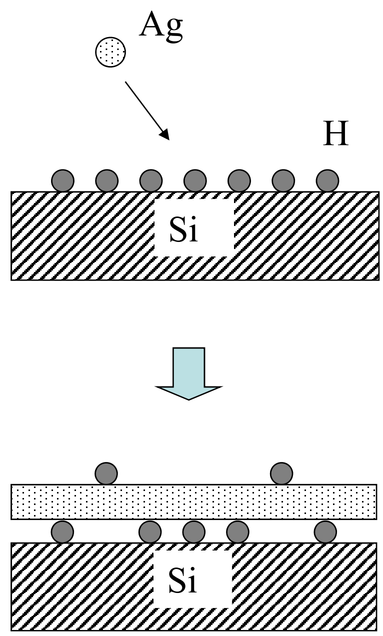
~ width/(dE/dz)

γ–ray spectrum



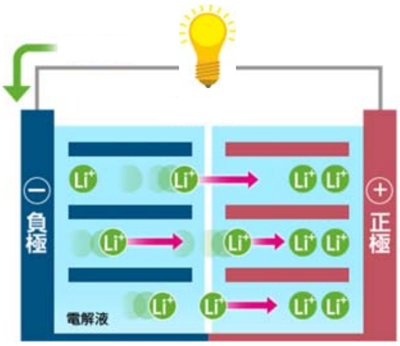
Depth distinction of H



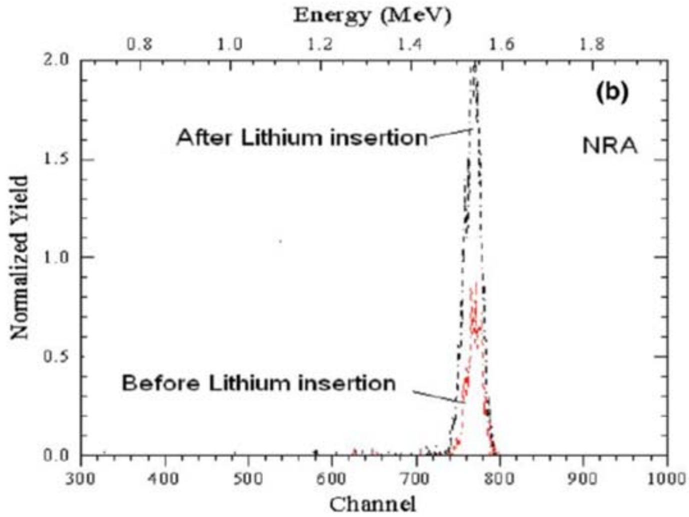


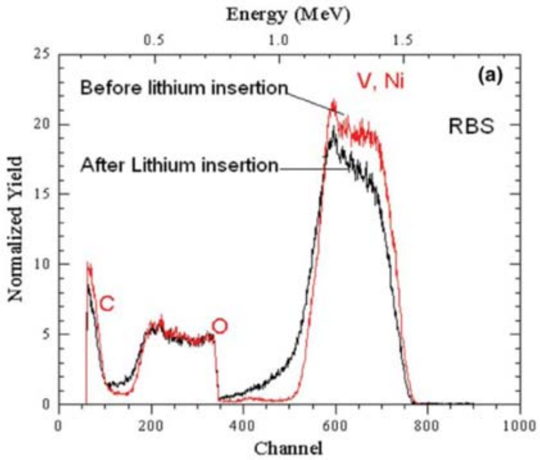
Phys. Rev. B59 (1999) 13020.

Li ion battery: transport of Li



$LiNiVO_4$ (300 nm)/C cathode





^{4}He (2 MeV) RBS

M.V. Reddy *et al.*, NIMB 246 (2006) 397

Hydrogen in solids: dual nature

∗ Electronic effects on host properties

H-induced metal-insulator transition

Relation with electric-device performance

∗ Proton motion

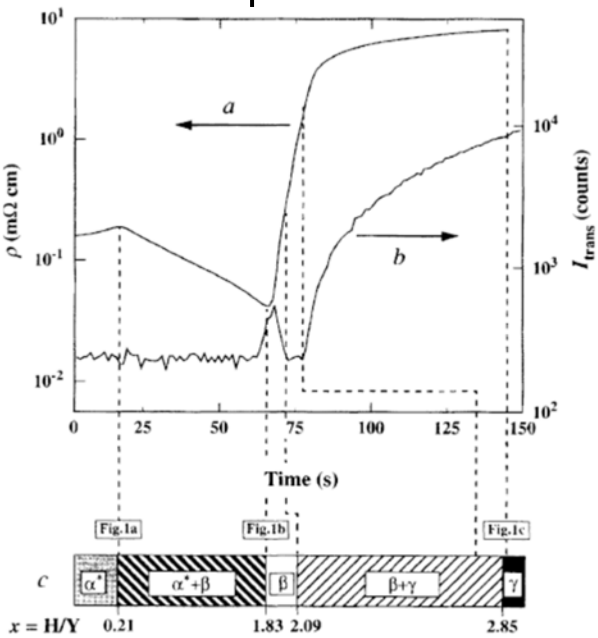
proton diffusion

hydrogenation reaction：photocatalysis

electronic to chemical energy conversion

H-induced metal insulator transition

Thin Y films (500 nm):
exposure to H

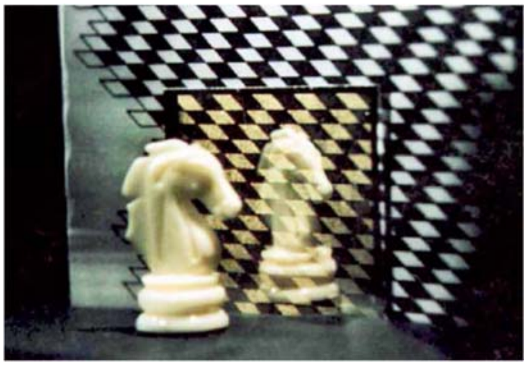


Metal → Insulator

(J. N. Huiberts et al., Nature 380, 231 (1996))

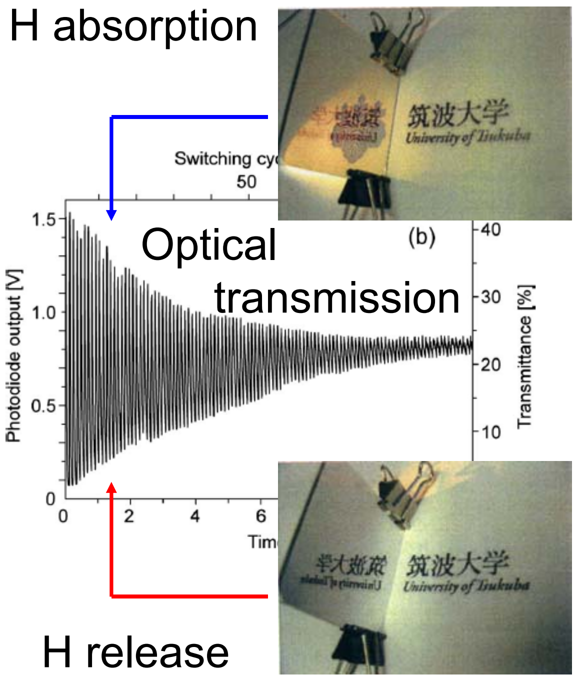
Mirror

Transparent



Degradation mechanism: MgNi hydride

H absorption



Optical transmission

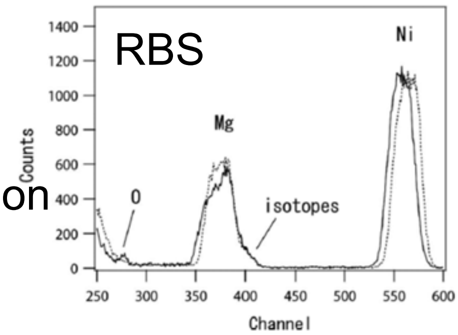
H release

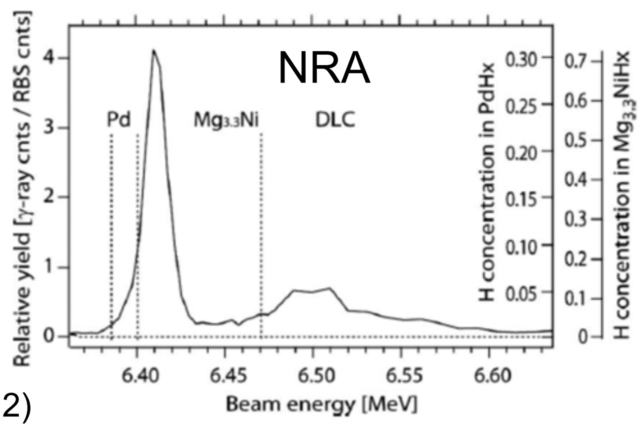
(D. Sekiba et al., JAP 106, 114912)

Mg segregation

↓

MgH_2 , MgO formation



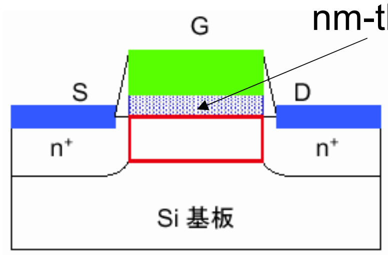


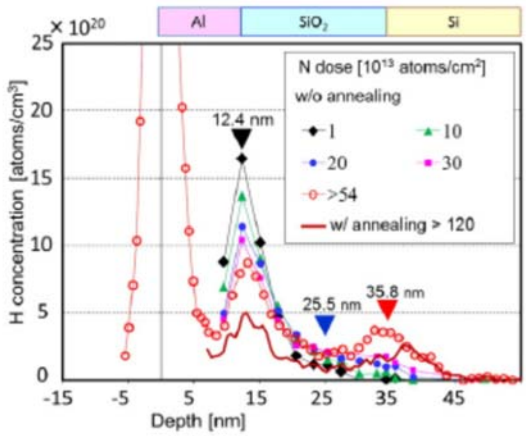
H in Si devices

Si devices

- MOS transistor
- Photo/ particle detector
- Solar cell

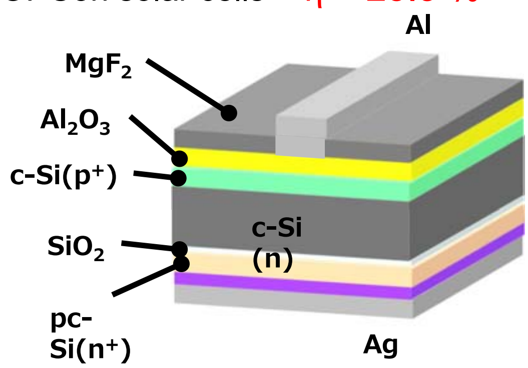
MOS transistor





MicroeleRel_70_12

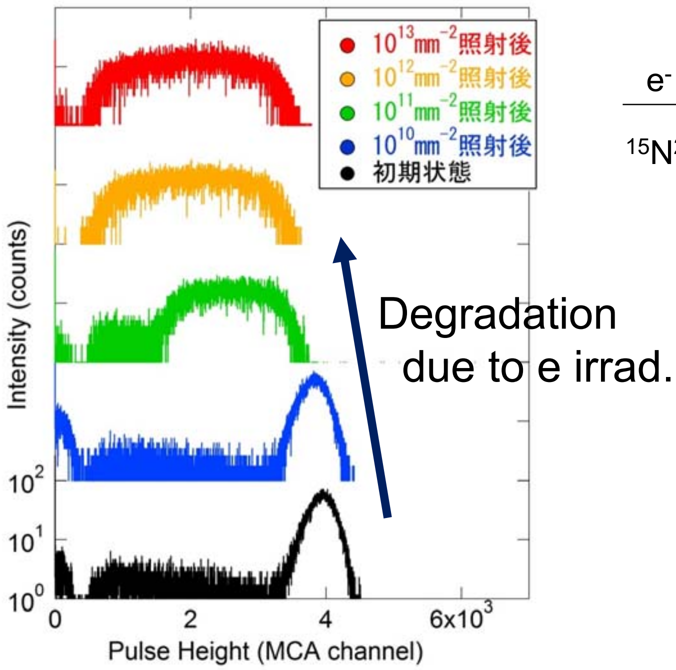
TOPCon solar cells η = 25.3 %



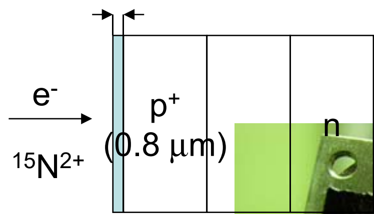
Appl._Phys._Express_11_102301

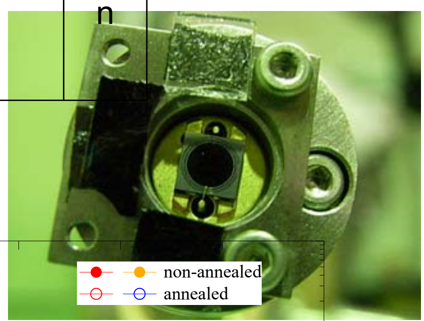
Degradation mechanism of Si detector

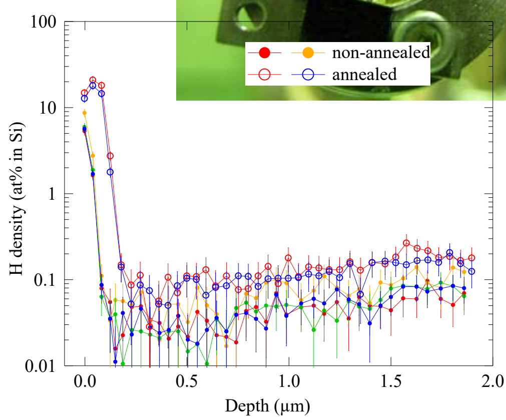
Pulse height analysis



IEEE EDL 33, 1162 (2012)







Hydrogen absorption in Pd

H_2 gas: large volume

Store H in metal, and extract when necessary

- How much H is in Pd?
- How stable is H in Pd?
- How fast is H absorption into Pd?
- Does absorbed H participate in reactions?

Hydrogen absorption:

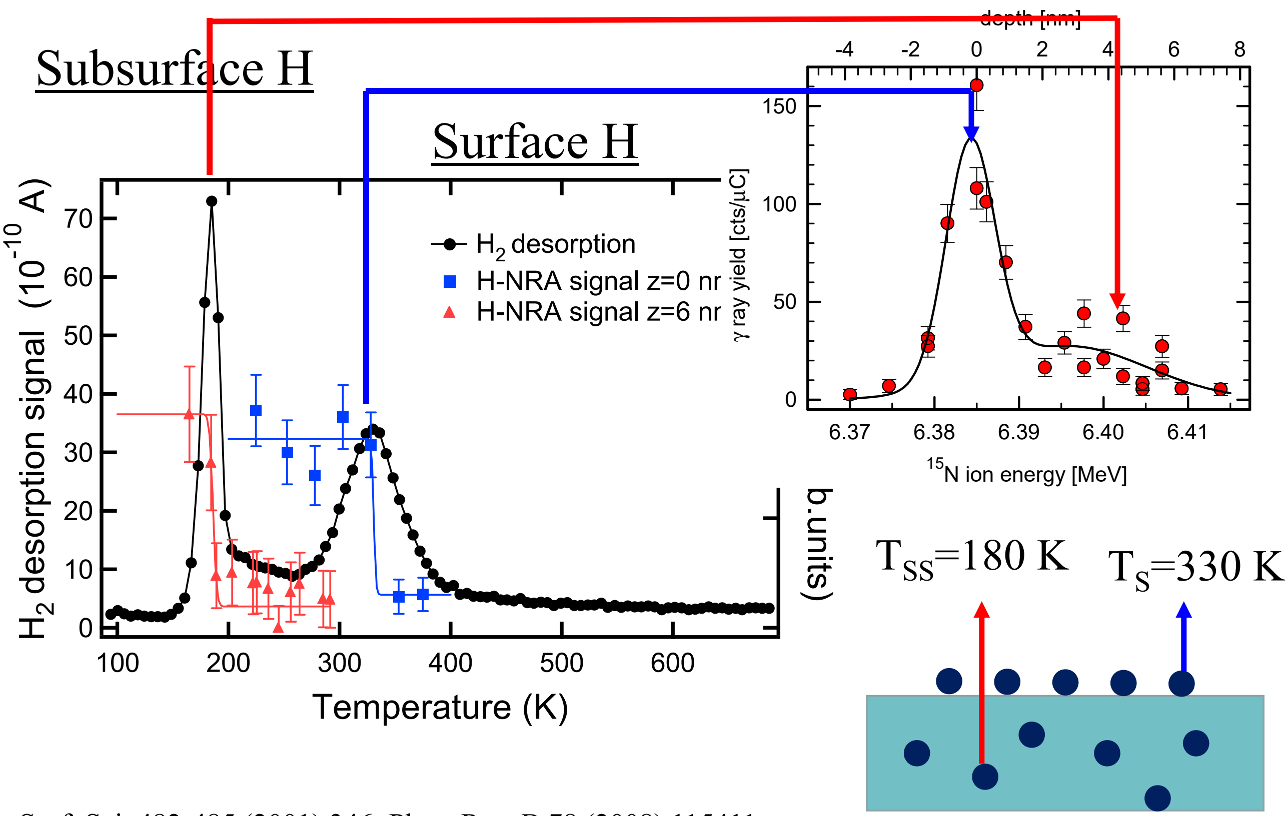
transport of H via surfaces

- **Absorption properties**
- **Surface properties**

→

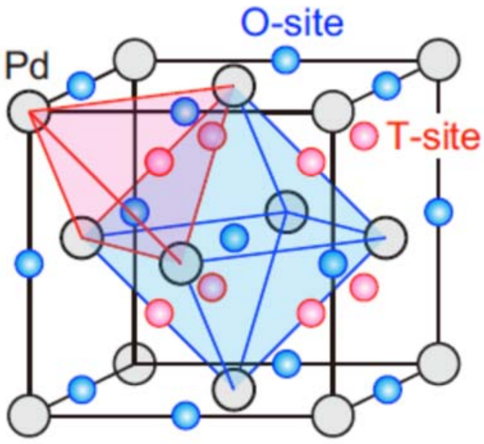
- **Nano particles**
- **Surface modification**

Absorption & release of H in Pd

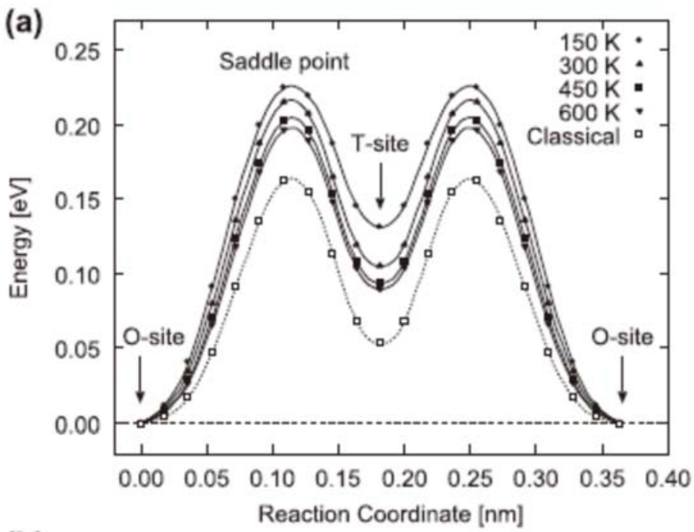


Surf. Sci. 482-485 (2001) 346; Phys. Rev. B 78 (2008) 115411.

H in interstitials of Pd



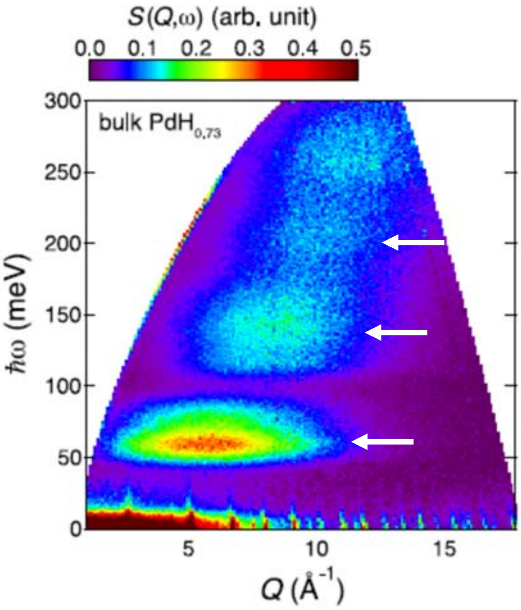
Calculated potential



- O-site: most stable
- T-site: metastable

Looks harmonic

Neutron inelastic scattering: H in Pd



Almost equally spaced peaks

Vibration of H

Z. Phys B 55, 283 (1984); PhysRevB.96.054304

3D harmonic oscillator

$$V(x,y,z) = C(x^2 + y^2 + z^2)$$

$$E = \sum_{i=x,y,z} \hbar\omega(n_i + \frac{1}{2}) \qquad |n_x n_y n_z\rangle$$

anharmonic term

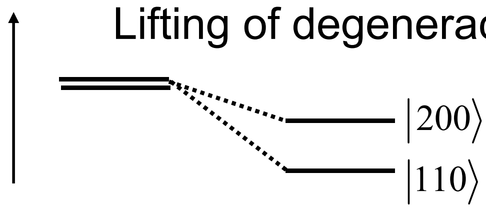
$$V' = C'(x^2y^2 + y^2z^2 + z^2x^2)$$

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a_x^\dagger + a_x)$$

perturbation

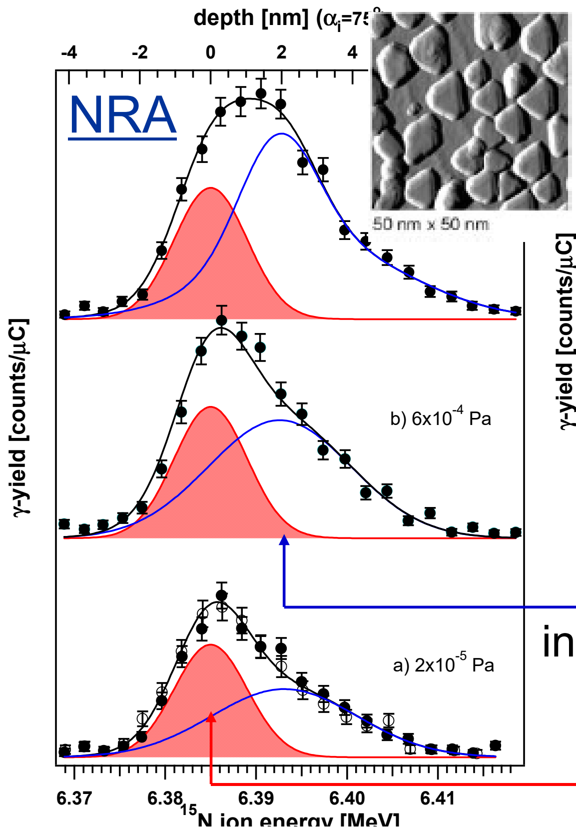
$$\langle 200|V'|200\rangle \neq \langle 110|V'|110\rangle$$

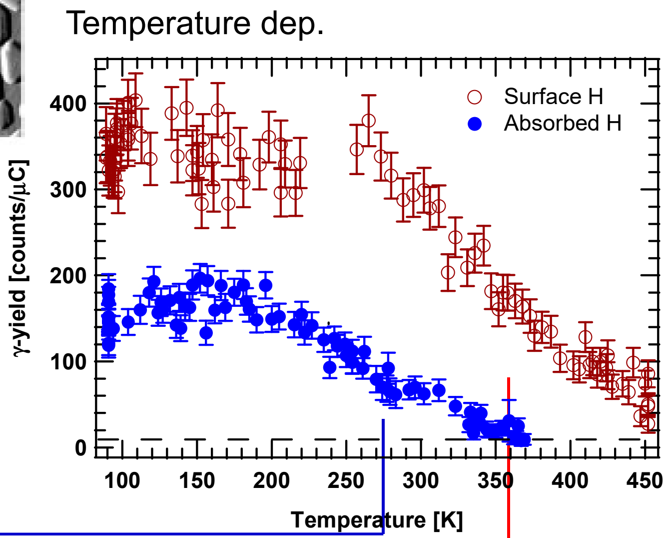
Lifting of degeneracy



H absorption in Pd nano particles

Phys. Rev. B 77, 113412 (2008)





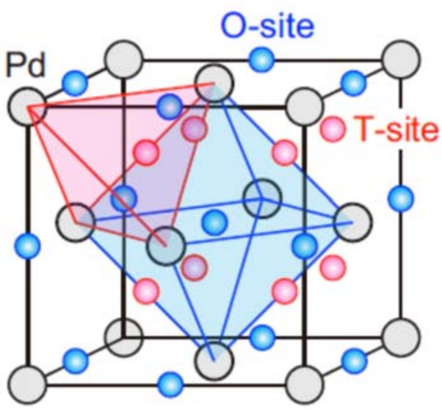
interior

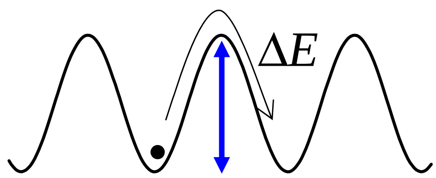
Td = 270K (cf. 180 K for Pd(100)

surface

Td = 360K

Diffusion of a particle





H undergoes hopping

from one site to neighboring sites

$$D = \Gamma \frac{\ell^2}{2d_s}$$

Γ : Jump rate

ℓ^2 : Mean sq. jump distance

d_s : dimension

Diffusion equation

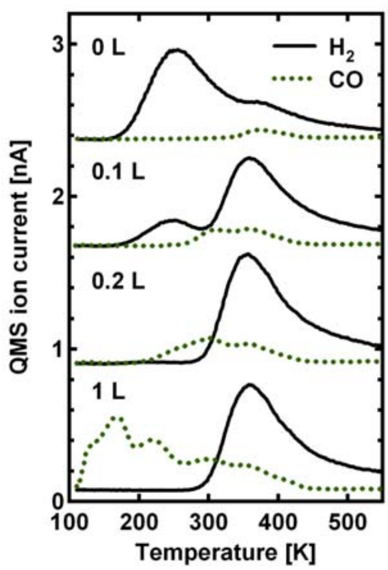
$$\frac{\partial c(\vec{r},t)}{\partial t} = D\nabla^2 c(\vec{r},t)$$

Thermal diffusion

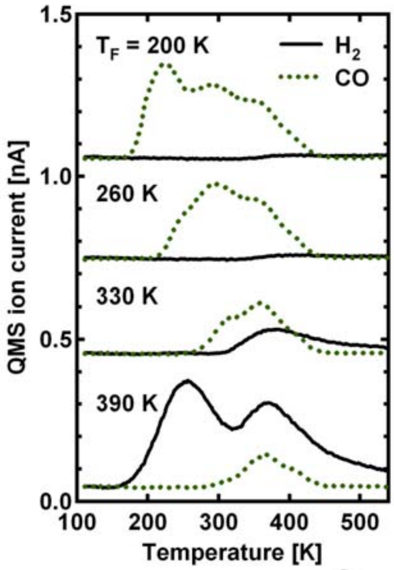
$$D = D_0 \exp(-\Delta E / kT)$$

Molecular cap by CO

CO → H/AuPd

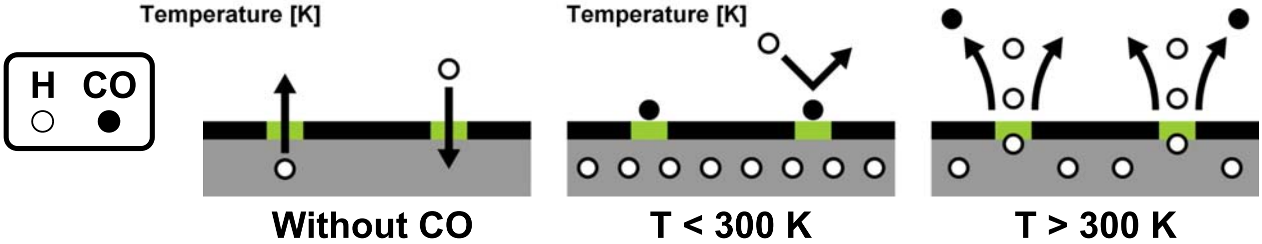


H_2 → CO/AuPd



1. CO blocks H_2 dissociation penetration

2. CO stabilizes absorbed H



(S. Ogura et al., J. Phys. Chem. C 117, 9366 (2013))

Stability & kinetics

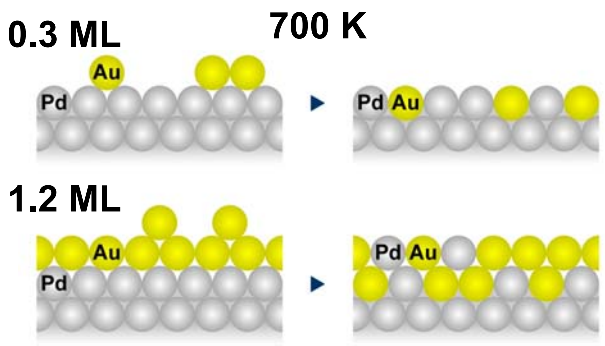
	desorption T		abs. prob.
	surface	subsurf.	
Pd	320 K	180 K	~7×10^{-4}
AuPd	—	250 K	~3×10^{-2}
Nano-Pd	360 K	270 K	
CO-cap		350 K	

Comapred with Pd

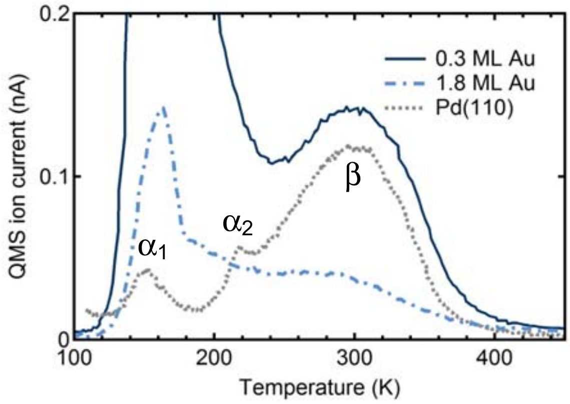
AuPd: lattice expansion

Pd nano particle: lattice deformation

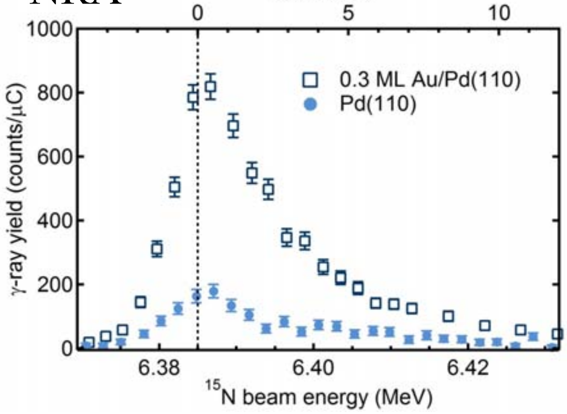
Surface modification by Au



TDS



NRA



α1：absorbed H

→ increase

β：surface-adsorbed H

→ decrease

K. Namba et al., PNAS 115, 7896 (2018)

Enhancement of H absorption by Au

Absorption probability

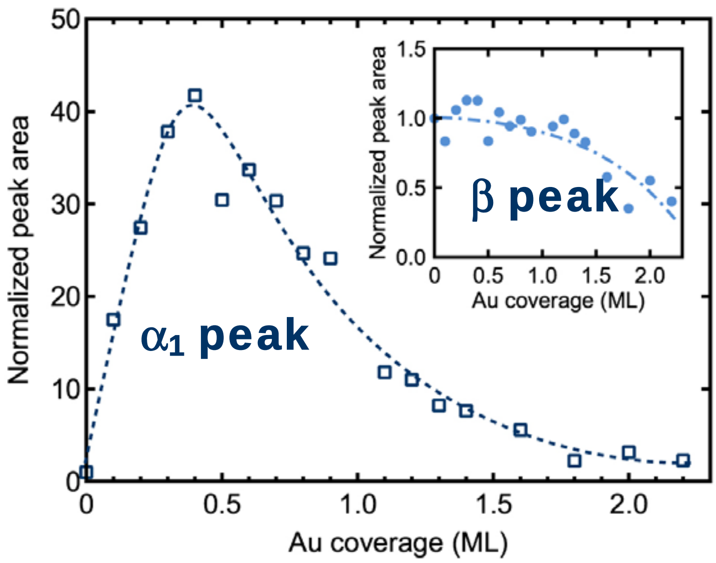
Max at θ_{Au}=40%

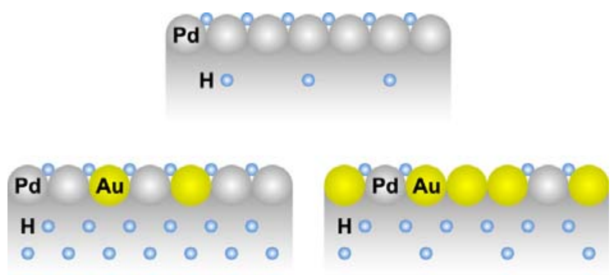
Decrease of Surf. H with increasing Au

"Conventional idea"

Au: chemically inert

→ useless for H absorption





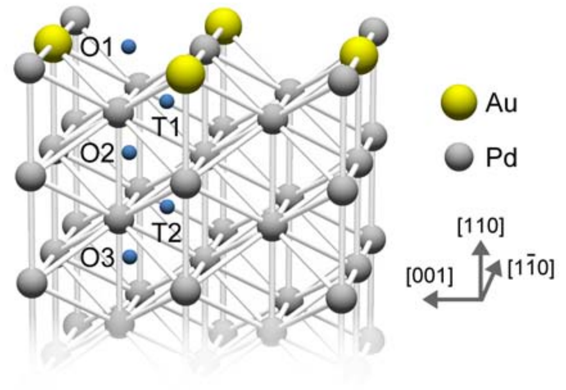
Role of Au for H absorption

First-principles total-energy cal.

(1) Adsorption on surface

(2) Diffusion into subsurface

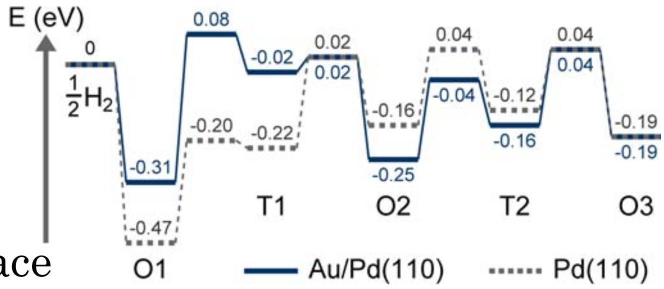
(3) Diffusion to bulk



Where is the bottleneck?

Surface destabilization
→ enhancement of (2)

Too much Au
→ no adsorption on surface

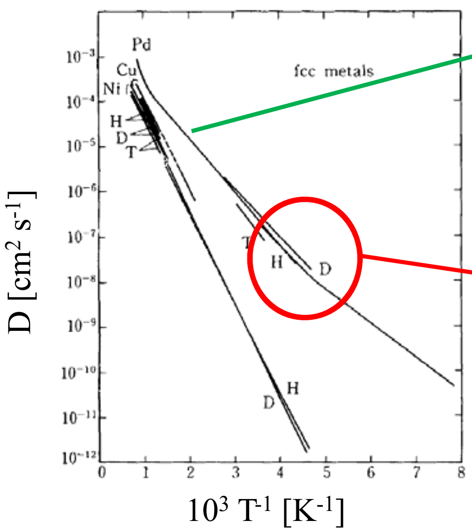


K. Namba et al., PNAS 115, 7896 (2018)

Quantum effects in diffusion

Diffusion coefficient

Temp. dep.



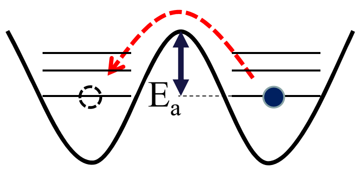
Y. Fukai, The Metal-Hydrogen System, Springer Series in Materials Science (2005).

High T

① Thermal diffusion

$D \propto \exp(-E_a/kT)$

Over barrier



② D is faster than H

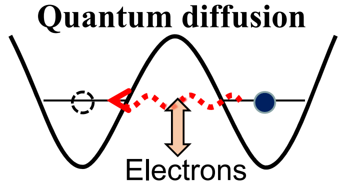
Inverse isotope effect

Low T

③ Quantum tunneling?

$D \sim const.$

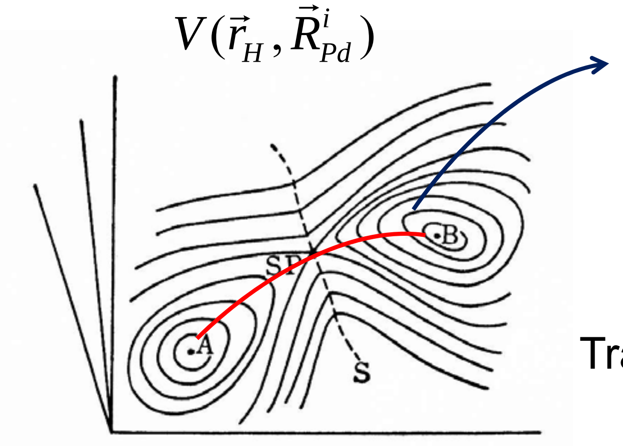
Quantum diffusion

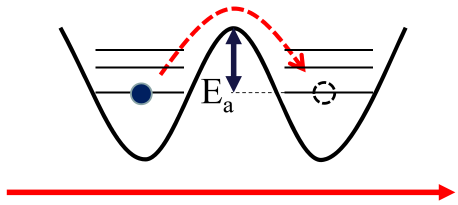


Origin of inverse isotope effect

Multi-dimensional potential

$$V(\vec{r}_H, \vec{R}^i_{Pd})$$



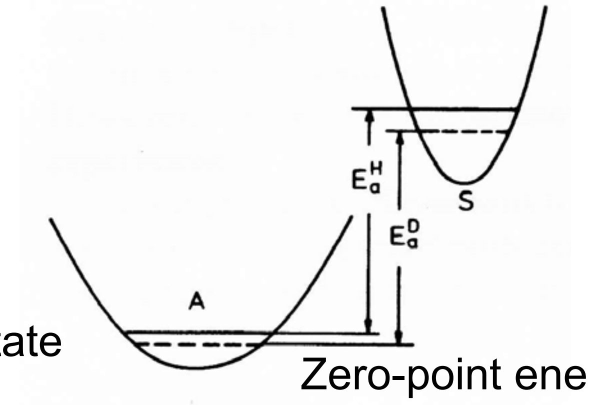


Reaction coordinate

Transition state = saddle point

If confinement at SP is strong,

$$E_a^H > E_a^D$$



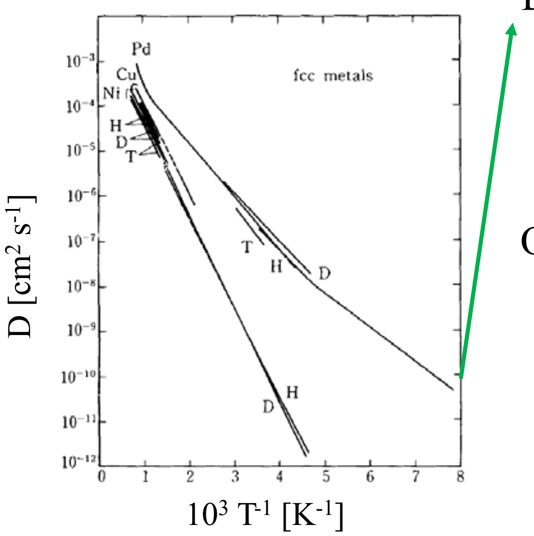
Initial state

Zero-point energy

Quantum effects in diffusion

Diffusion coefficient

Temp. dep.

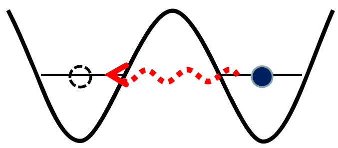


Y. Fukai, The Metal-Hydrogen System, Springer Series in Materials Science (2005).

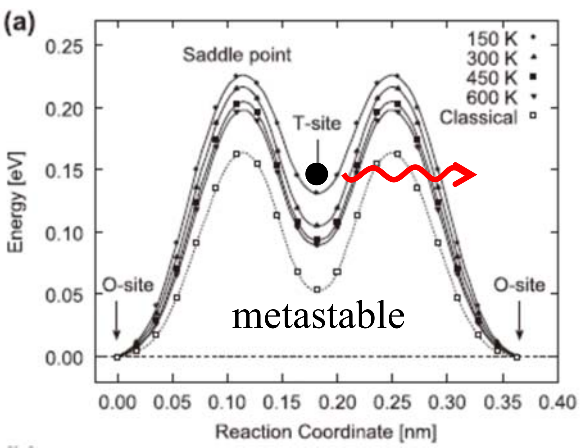
Low T: no data

③ Quantum tunneling?

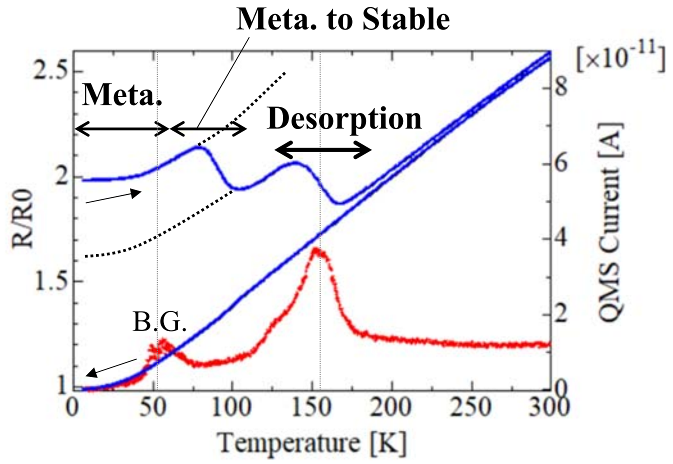
$$D \sim const.$$

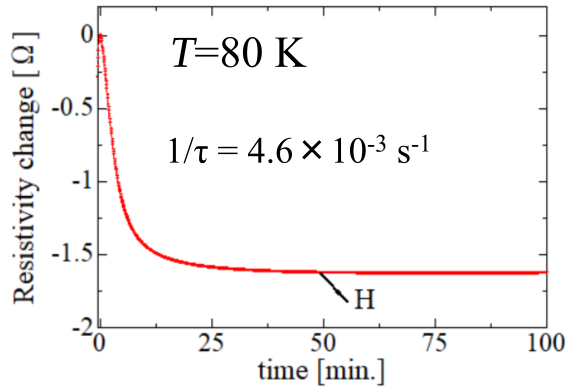


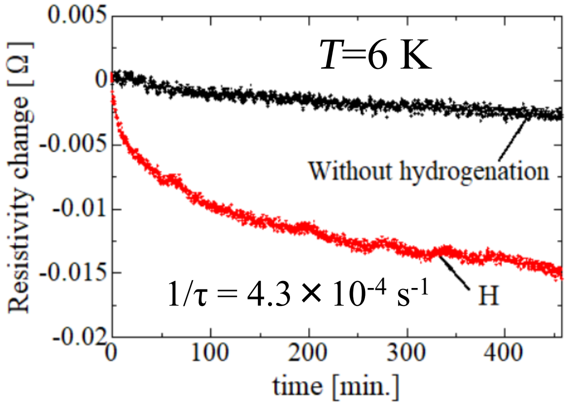
Our recent strategy: T to O diffusion



Probing H diffusion by resistance







H ion implantation
→ T-site occupation

Resistance change
by H diffusion from T to O

T. Ozawa et al., Vac. Surf. Sci. in press.

Temperature dependence of H/D hopping rate

$\exp(-E_a/kT)$

① Thermal diffusion above 80 K

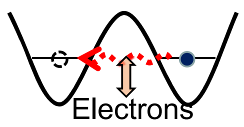
② Normal isotope effect

③ small T dependence

Isotope dependence

Proton tunneling

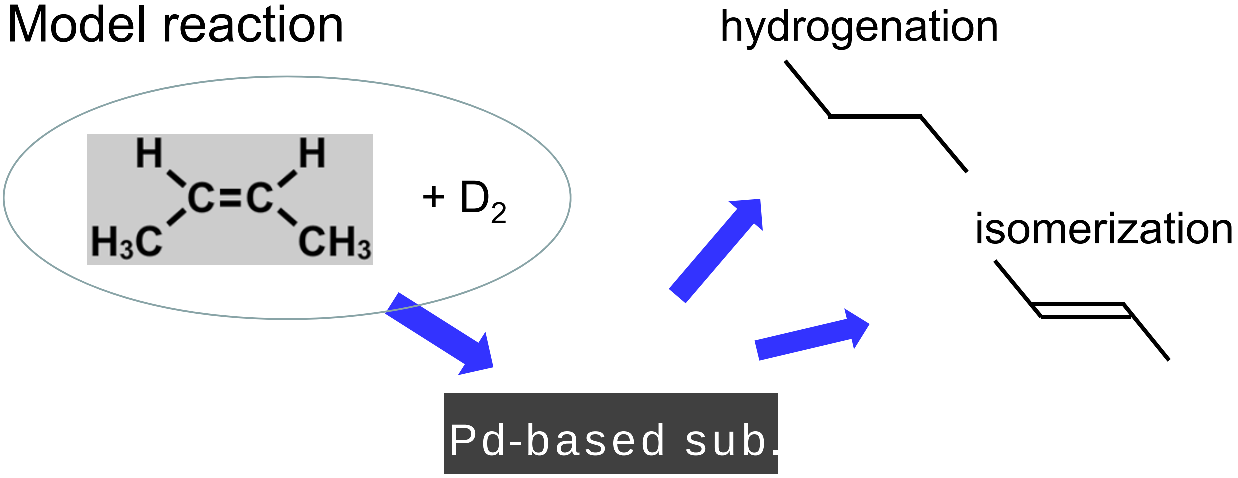
Coupling with electrons



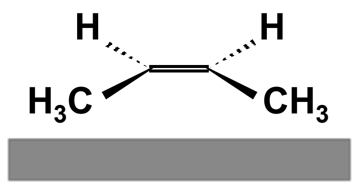
Cf. J. Kondo, Physica 125B (1984) 279.

Reaction: hydrogenation & isomerization

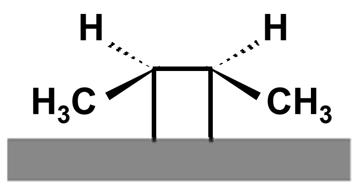
Model reaction



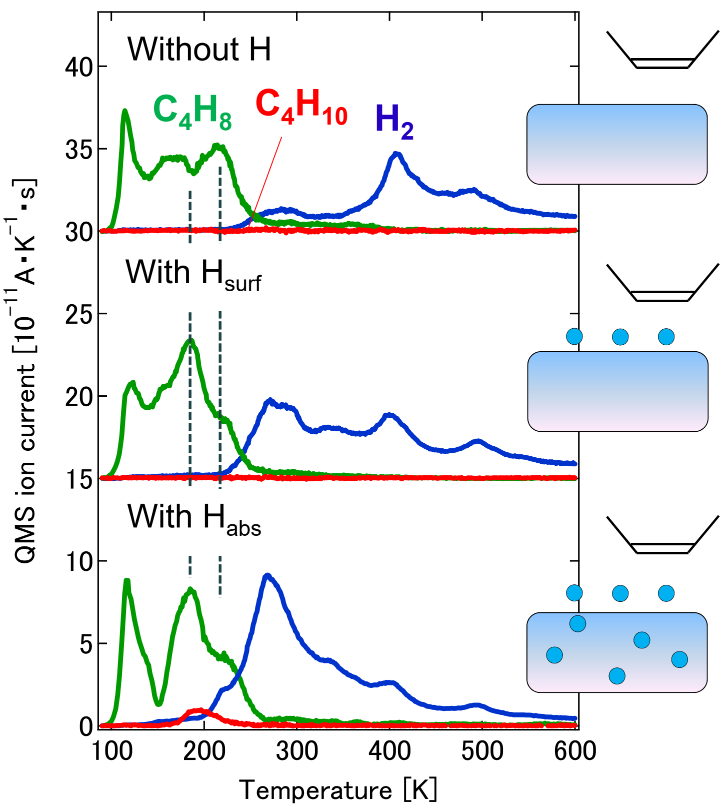
π bond



di-σ



Reaction TPD: C_4H_8 + H on Pd(110)



H_2 desorption:
⇒ C_4H_8 decomposition

LT desorption of C_4H_8
⇒ modification of C_4H_8

C_4H_{10} production

Summary

Use of Quantum beams (e^-, Ion, Neutron, Muon)

for materials analysis

Elastic & Inelastic scattering by materials

information on atomic & electronic structures

→ origin of material functions

Application: analysis of H

Electronic effect: metal and semiconductor

Proton motion: Energetics, dynamics, kinetics

Quantum effects and chemical reaction