ELECTRONIC STOPPING OF SLOW PROTONS IN OXIDES

<u>Dietmar Roth</u>, Barbara Bruckner, Andrei Ionut Mardare, Christina L. McGahan, Meirzhan Dosmailov, J. Iñaki Juaristi, Maite Alducin, Daniel Primetzhofer, Richard F. Haglund, Johannes D. Pedarning, and Peter Bauer

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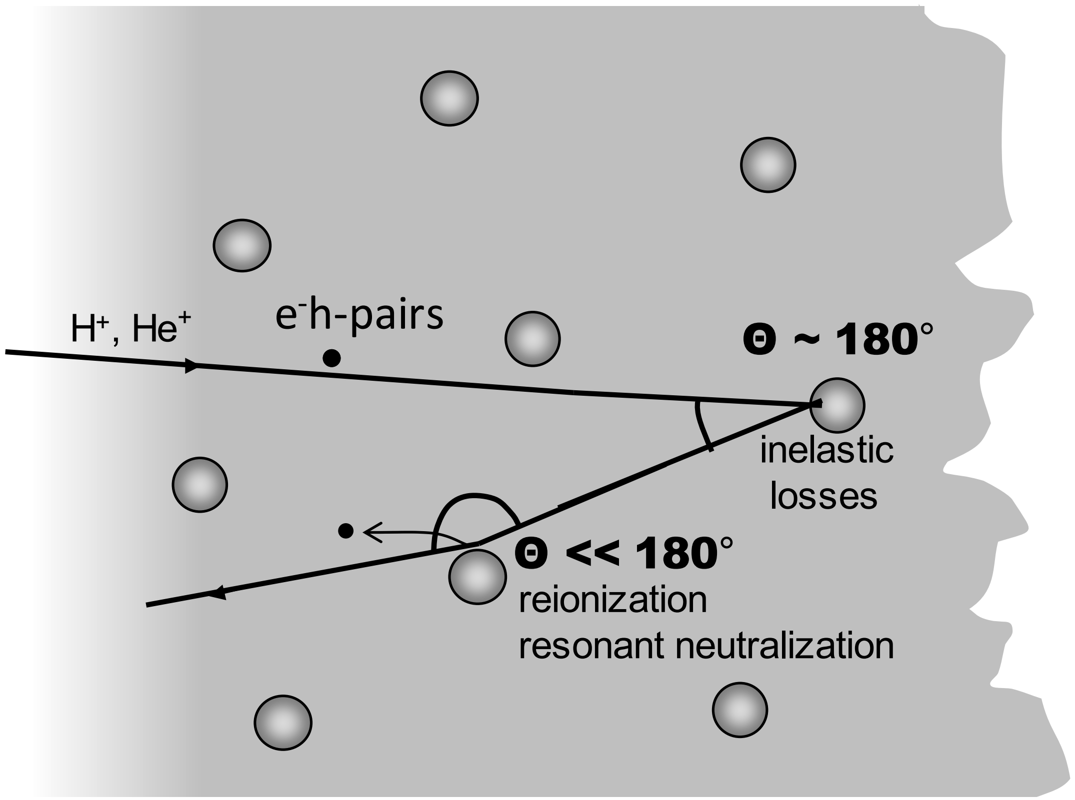
JOHANNES KEPLER
UNIVERSITÄT LINZ

atom und
oberflächen
physik

OUTLINE

- Interactions of ions with a solid
- Evaluation of LEIS spectra
- Electronic stopping: band structure effects in noble metals and insulators
- Electronic stopping of H^+ in oxides
- Summary

INTERACTIONS OF IONS WITH A SOLID



- ■ Large angle scattering
- ■ Charge exchange
- ■ Deceleration of ions
  - ☐ due to interaction with nuclei
  - ☐ due to interaction with electrons

“Electronic and nuclear stopping“

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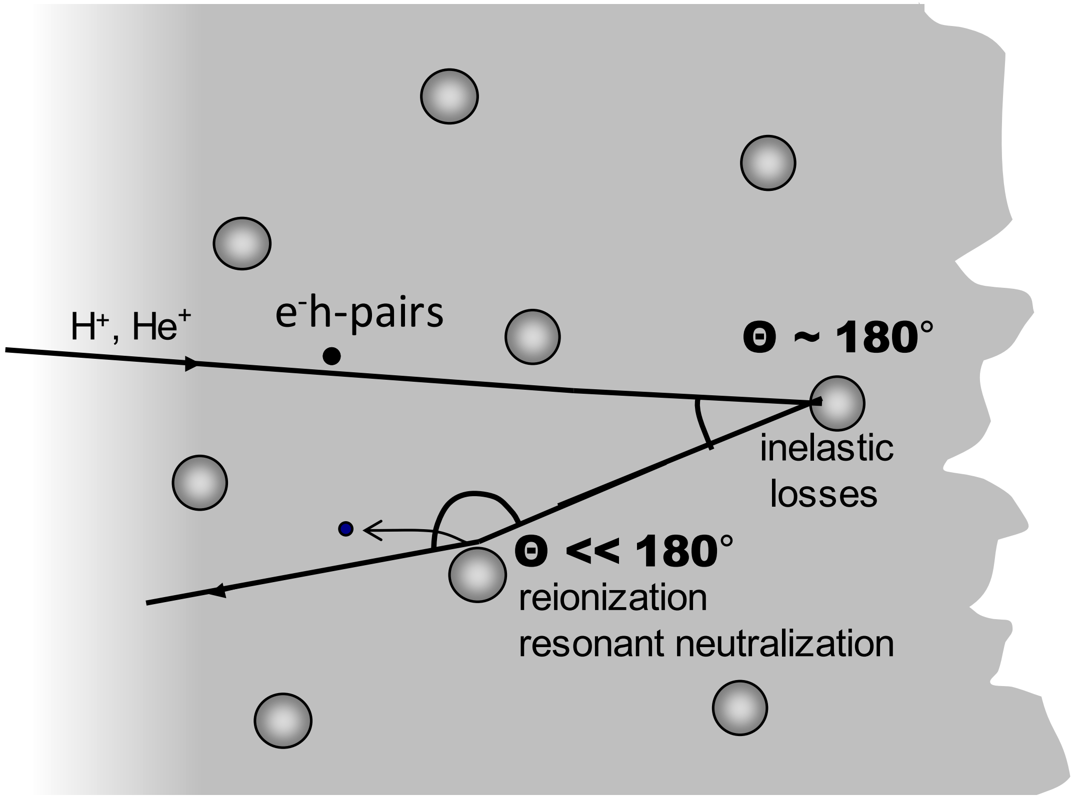
ELECTRONIC STOPPING IN A SOLID



- Stopping power $S = -\frac{dE}{dx}$
- slow ions ($v \leq v_F$): **interaction with valence electrons**
- **slow ion ≡ strong pertubation**
- theory: free electron gas (FEG)

$$S = Q(Z_1, r_s)v$$

Fermi & Teller, PR 72, 399-408 (1947)
Non-linear model: Echenique et al., PRA 33, 897-904 (1986)

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ELECTRONIC ENERGY LOSS: DEFINITIONS

- stopping power $S = -\frac{dE}{dx}$

- stopping cross section $\varepsilon = -\frac{1}{n}\frac{dE}{dx}$

  - ☐ elemental target materials: n … number of atoms/cm^3
  - ☐ compound materials (X_AY_B): n … number of molecules/cm^3

- **molecular density: ε depends only on electronic properties of the molecule**
  but: number of valence electrons $N_{val} \leftrightarrow$ size of the molecule

LOW ENERGY ION SCATTERING

Yield of backscattered projectiles:
(single scattering approximation)

$$Y_{BS} = N_0 \cdot n\Delta x \cdot \frac{d\sigma}{d\Omega} \cdot \Omega \cdot \eta$$

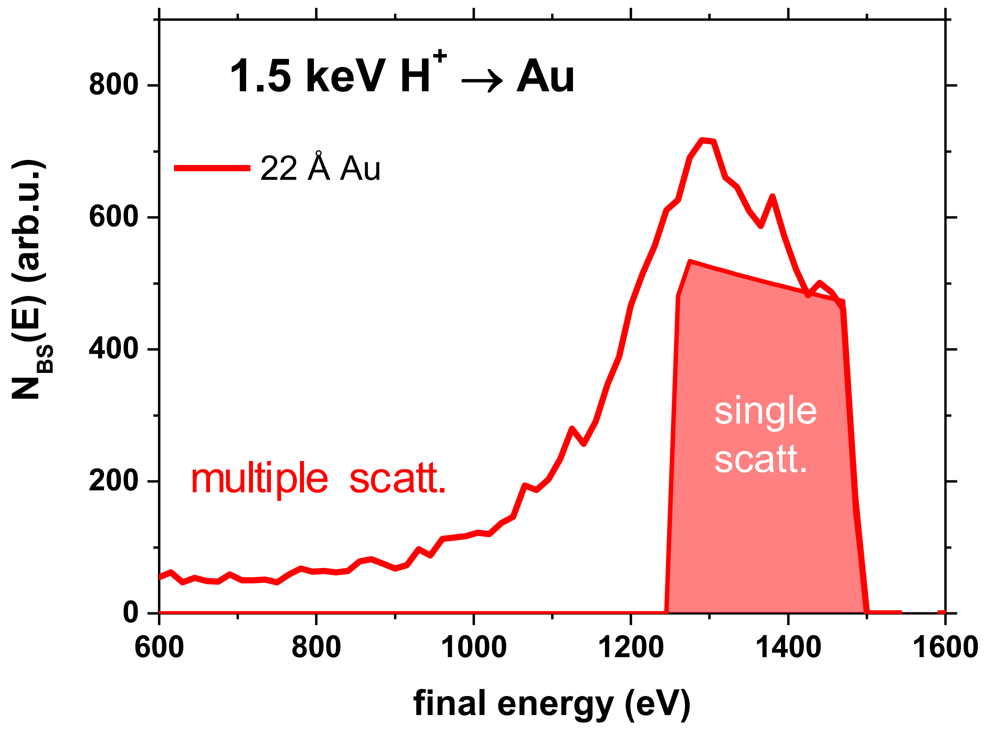
N_0 … primary ion charge

n … atomic concentration

$d\sigma/d\Omega$ …scattering cross sect. ($V(r) = V_c(r)\phi(r/a)$)

Ω … detector solid angle

η … detector efficiency



Large scattering cross section - multiple scattering important in LEIS

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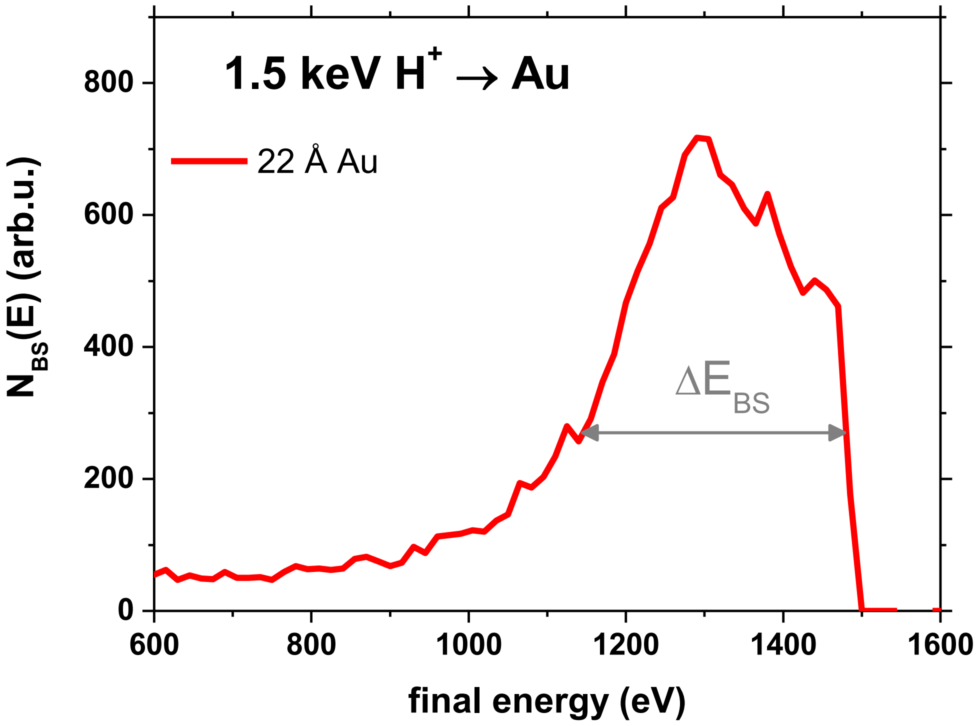
LOW ENERGY ION SCATTERING

Width of energy spectrum:
(single scattering approximation)

$$\Delta E_{BS} = \left[\frac{k}{\cos\alpha} \varepsilon\big|_{E_0} + \frac{1}{\cos\beta} \varepsilon\big|_{kE_0} \right] \cdot n\Delta x$$

$$\Leftrightarrow \quad \Delta E_{BS} \equiv [\varepsilon]\, n\Delta x$$

$[\varepsilon]$ …stopping cross section factor



Electronic and nuclear stopping may contribute to $[\varepsilon]$

LOW ENERGY ION SCATTERING

Height of energy spectrum:
(single scattering approximation)

$$H_{BS}(E) = \frac{\Delta Y_{BS}}{\Delta E_{BS}} = \frac{N_0}{\cos\alpha} \frac{d\sigma / d\Omega}{[\varepsilon]} \cdot \Omega \eta(E)$$

N_0 … primary ion charge

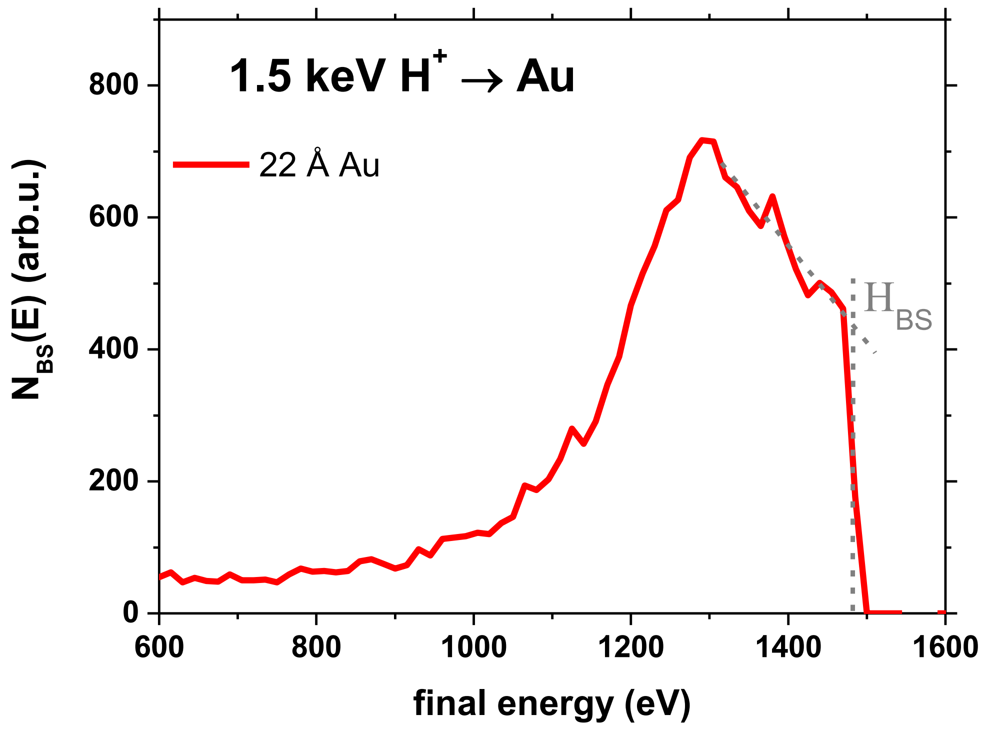
n … atomic concentration

$d\sigma/d\Omega$ …scattering cross section

$[\varepsilon]$ …stopping cross section factor

Ω … detector solid angle

η … detector efficiency



Multiple scattering and nuclear losses in LEIS
→ Data evaluation has to rely on MC simulations

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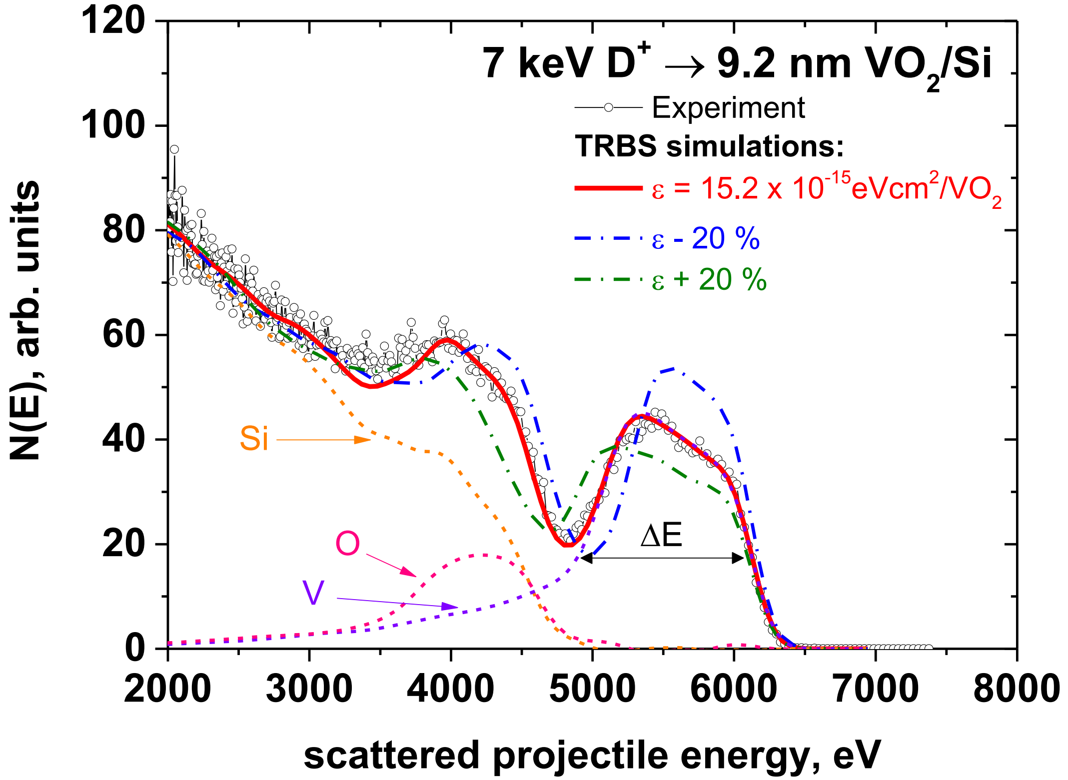
DATA EVALUATION: ULTRA-THIN FILMS



- thickness calibration with RBS
- comparison to Monte Carlo simulations (TRBS)
- variation of ε → change in width of vanadium peak ($\Delta E \propto [\varepsilon]$)

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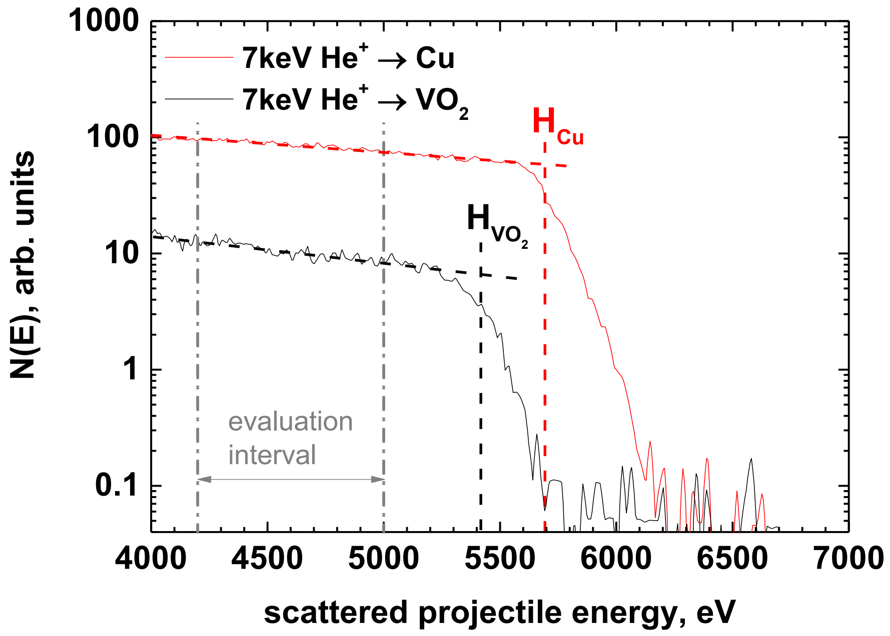
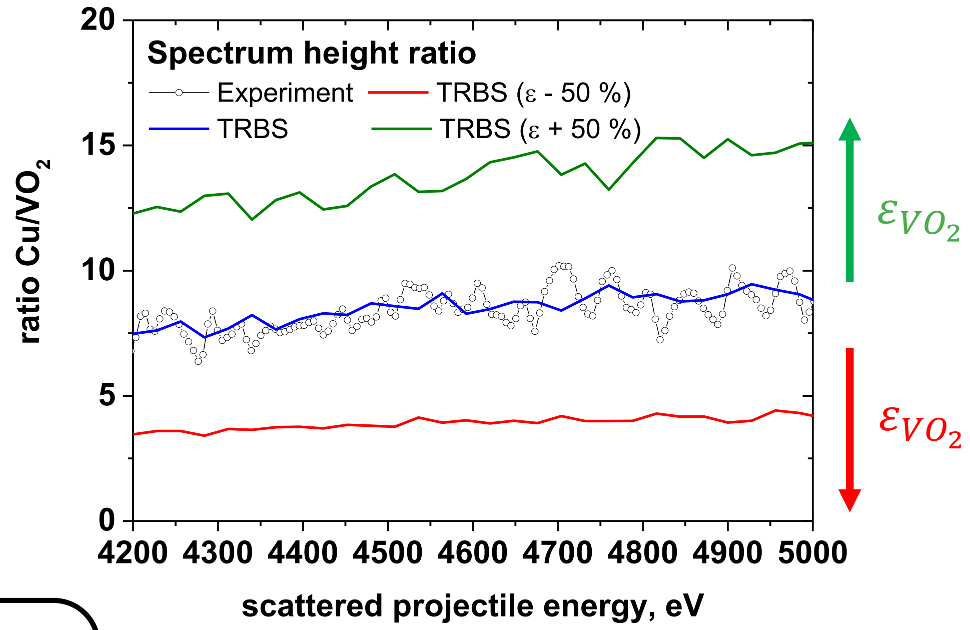
DATA EVALUATION: THICK SAMPLES





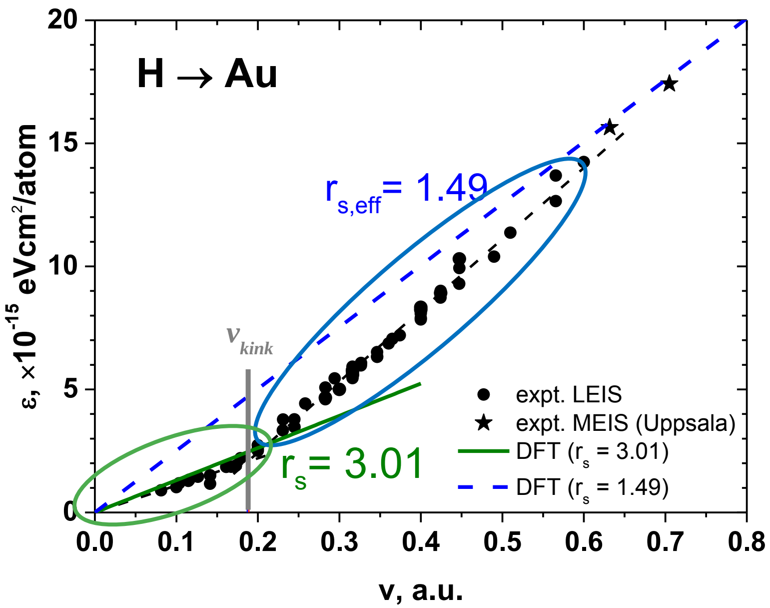
Comparison between height ratios of experiment and TRBS simulations

$$\frac{H_{Cu}}{H_{VO_2}} = \frac{\left(\frac{d\sigma}{d\Omega}\right)_{Cu}}{\left(\frac{d\sigma}{d\Omega}\right)_{VO_2}} \frac{[\varepsilon]_{VO_2}}{[\varepsilon]_{Cu}}$$

Reference material: Cu

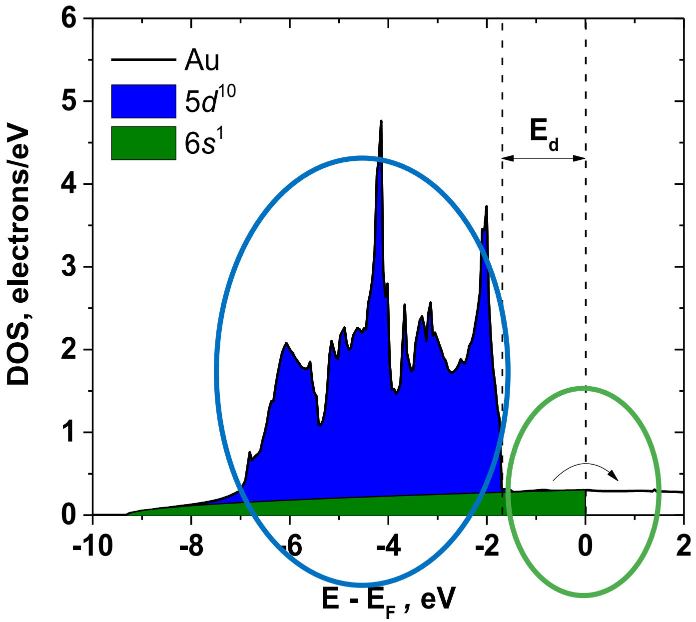
ELECTRONIC STOPPING IN NOBLE METALS: „kink“ in stopping cross section

- Experiment: slow H^+ in Au $\leftrightarrow \mathrm{d}E/\mathrm{d}x \neq Qv$



LEIS: S.N. Markin et al., PRB 78, 195122 (2008)
MEIS: D. Primetzhofer, PRB 86, 094102 (2012)

- DFT calculation of density of states (DOS)



M. Alducin (2016)

Au: FEG + *d*-electrons

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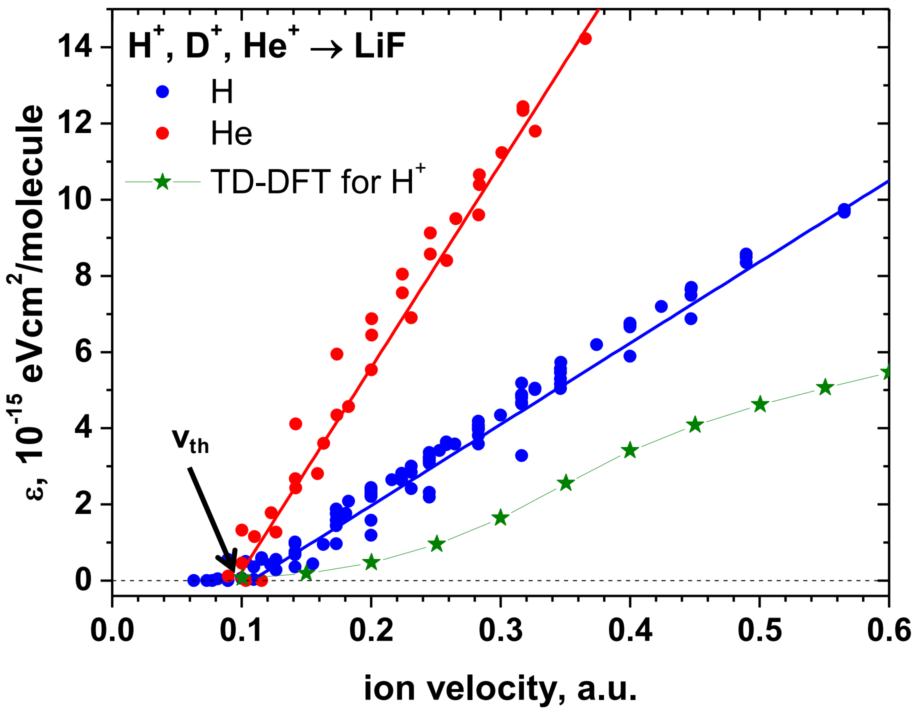
ELECTRONIC STOPPING IN INSULATORS: velocity threshold



Experiment: S.N. Markin et al., PRL 103, 113201 (2009)
TD-DFT calculation: Pruneda et al., PRL 99, 235501 (2007).

- LiF: band gap E_g = 14 eV
- $v < v_{th}$: $(dE/dx)_{electr.} = 0$
- v_{th} lower than expected from e-h pair excitation (TD-DFT)

Different channel for electronic energy loss in insulators?

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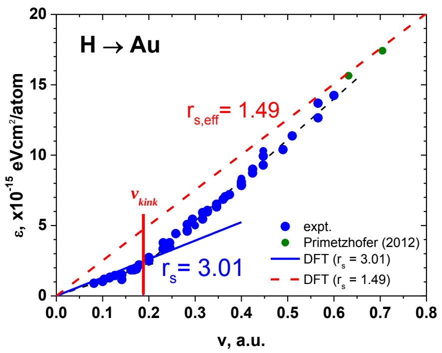
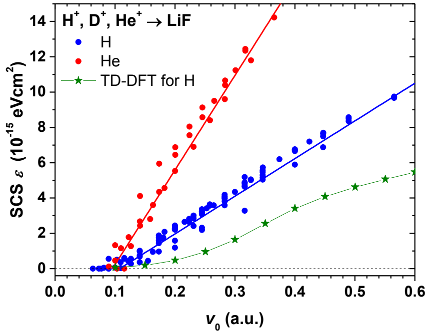
BAND STRUCTURE EFFECTS IN ELECTRONIC STOPPING

noble metals → ? → insulators





band gap

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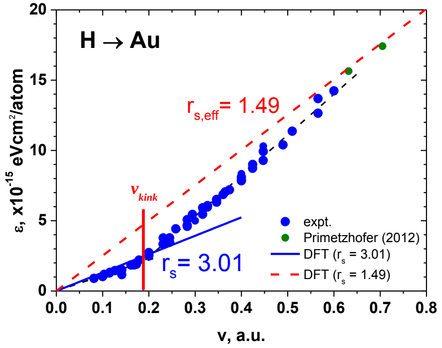
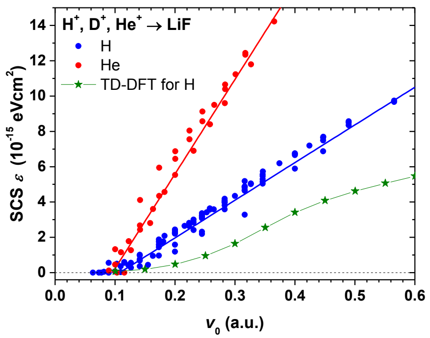
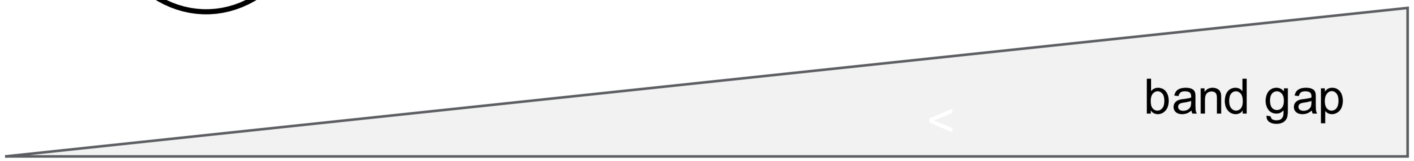
BAND STRUCTURE EFFECTS IN ELECTRONIC STOPPING

noble metals → oxides → insulators



VO_2	ZnO	Ta_2O_5	HfO_2	Al_2O_3	SiO_2
0 eV 0.7 eV	3.4 eV	4.5 eV	5.5 eV	8 eV	9 eV





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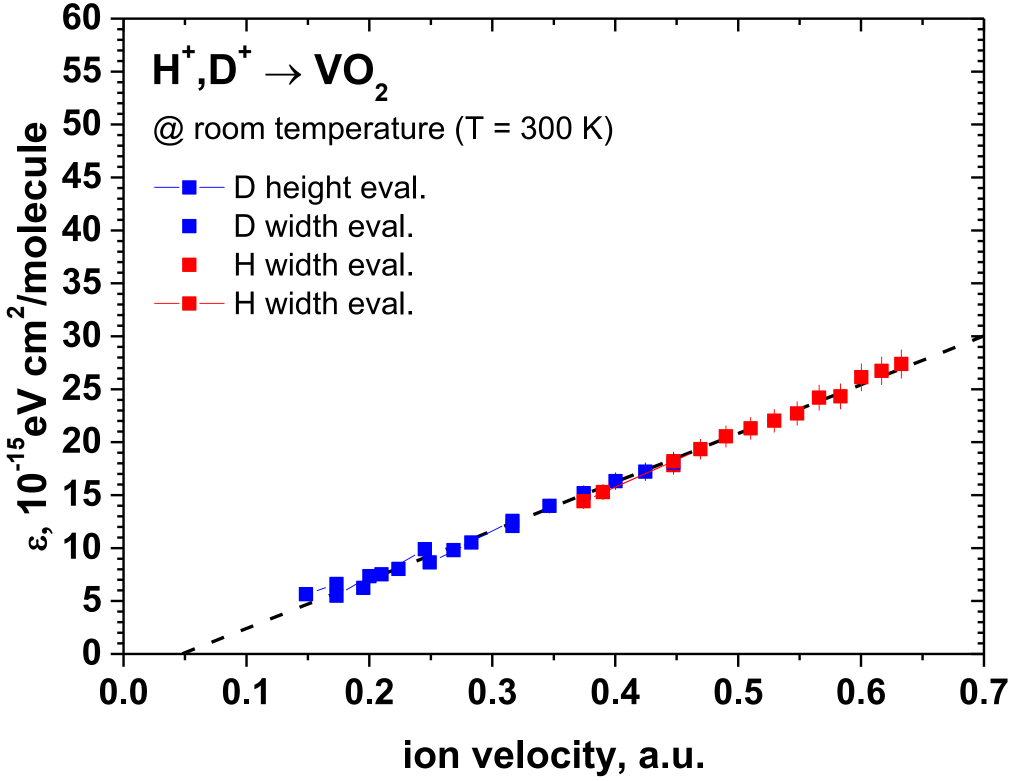
ELECTRONIC STOPPING OF H^+ IN VO_2: *ε* per molecule



- Reversible metal-to-insulator phase transition at ~ 340 K

- LEIS measurements at
  - ☐ 300 K: semiconductor
  - ☐ 373 K: metal

Different ε in metal and semiconductor?

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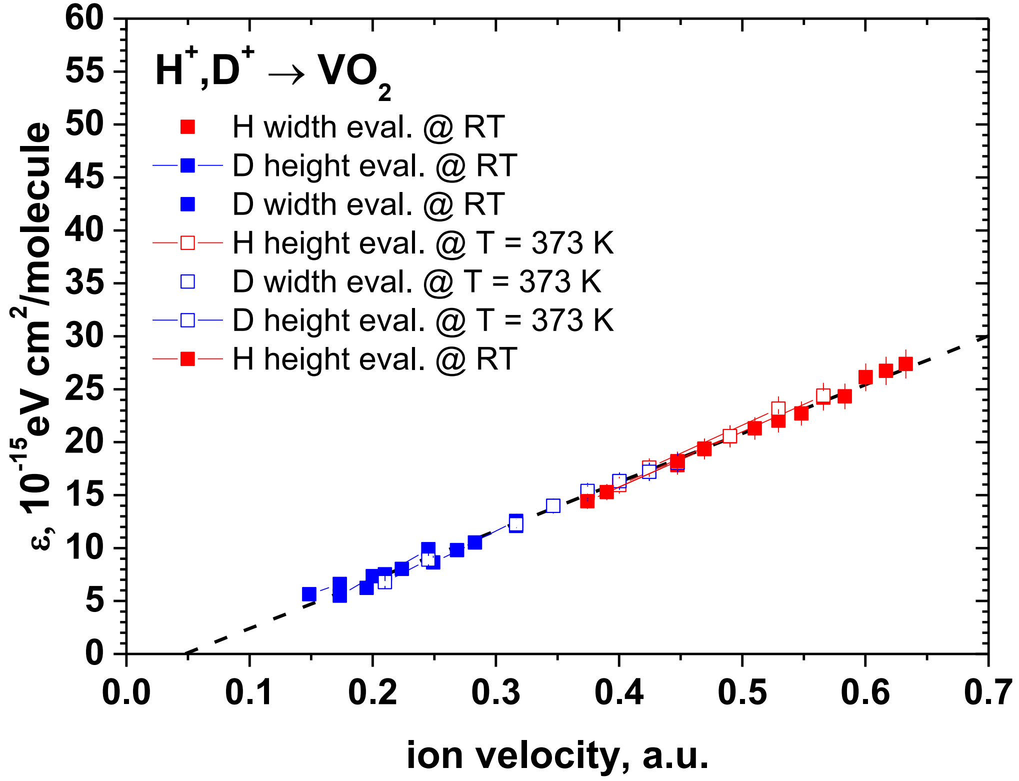
ELECTRONIC STOPPING OF H^+ IN VO_2: *ε* per molecule



- Reversible metal-to-insulator phase transition at ~ 340 K
- LEIS measurements at
  - 300 K: semiconductor
  - 373 K: metal

Same ε observed for metal and semiconductor!

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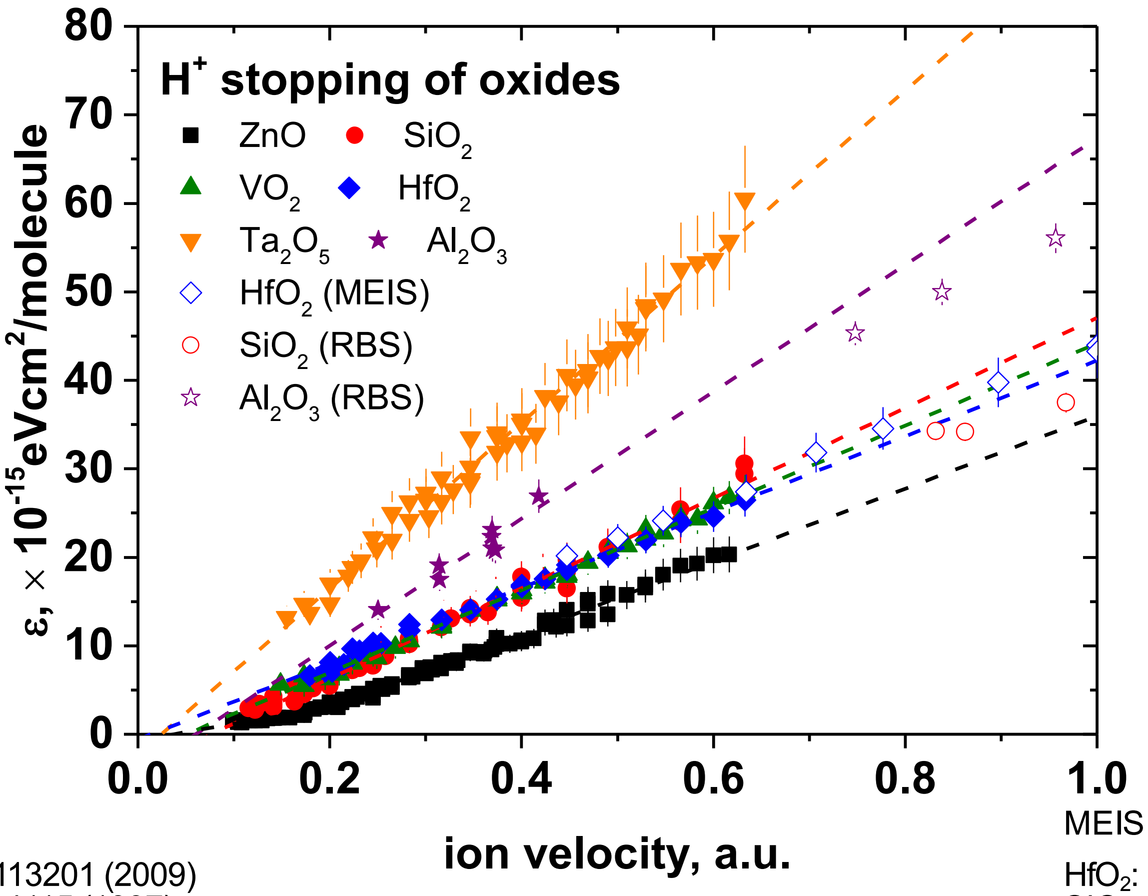
ELECTRONIC STOPPING OF H+ IN OXIDES: ε per molecule



Low velocity data:

SiO_2: S.N. Markin et al., PRL 103, 113201 (2009)
Al_2O_3: K. Eder et al., PRL 78, 4112-4115 (1997)

MEIS and RBS data:

HfO_2: D. Primetzhofer, NIMB 320, 100-103 (2014)
SiO_2 and Al_2O_3: P. Bauer et al. NIMB 69, 46 (1992)

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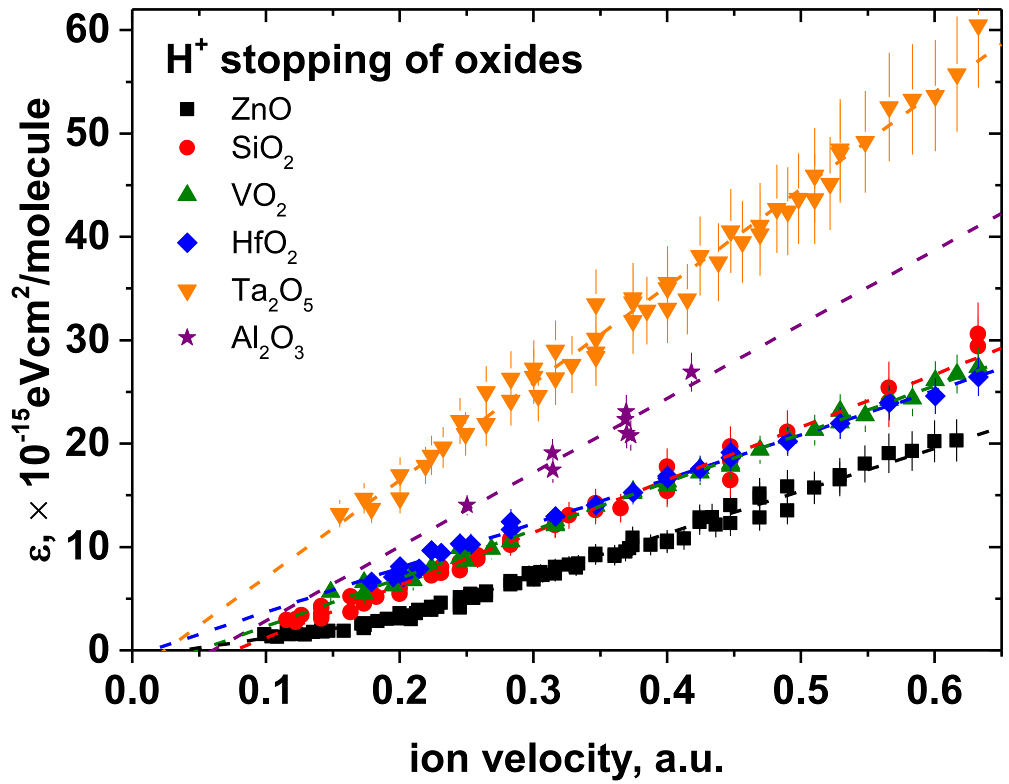
ELECTRONIC PROPERTIES OF SELECTED OXIDES: How do they influence dE/dx?

	E_{gap} (eV)	N_{val}	r_s (a.u.)	$\hbar\omega_{p,th}$ (eV)	$\hbar\omega_{p,expt}$ (eV)
VO_2	0 … 0.7	13	1.55	24	26
ZnO	3.4	6	2.13	15	18
Ta_2O_5	4.5	30	1.69	21.5	16
HfO_2	5.5	12	1.69	21	15
Al_2O_3	8	18	1.57	24	22
SiO_2	9	12	1.72	21	23

ELECTRONIC STOPPING OF H^+ IN OXIDES: ε per molecule $\leftrightarrow$ band gap?



SiO_2 data: S.N. Markin et al., PRL 103, 113201 (2009)
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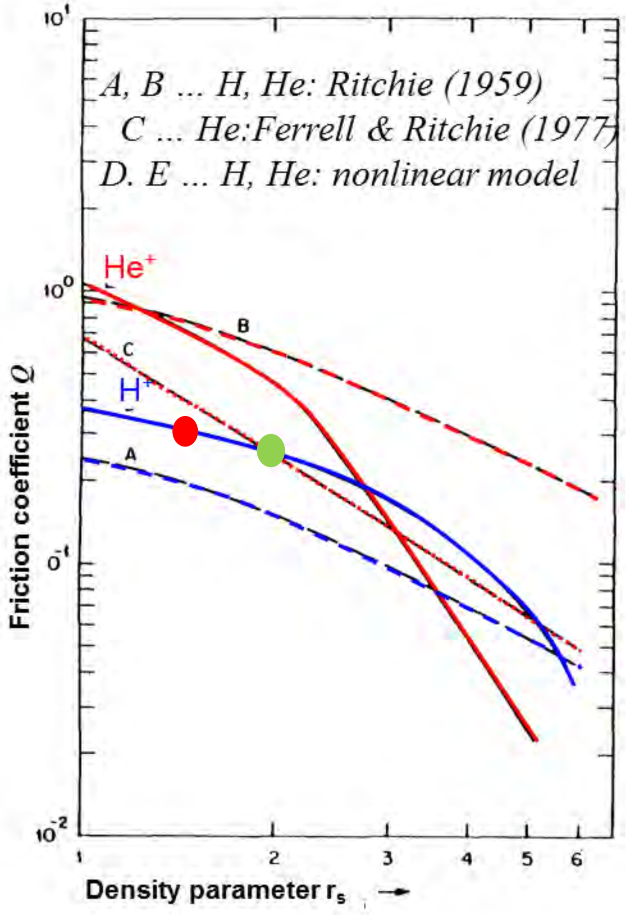
ELECTRONIC STOPPING OF H^+ IN OXIDES: Free Electron Gas model?



P.M. Echenique et al., PRA 33, 897-904 (1986)

$$S = Q(Z_1, r_s)v$$

	r_s (a.u.)	$\hbar\omega_{p,th}$ (eV)	$\hbar\omega_{p,expt}$ (eV)
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$$r_{s,eff} = \left(\frac{47.1}{\hbar\omega_{p,expt}(eV)}\right)^{2/3}$$

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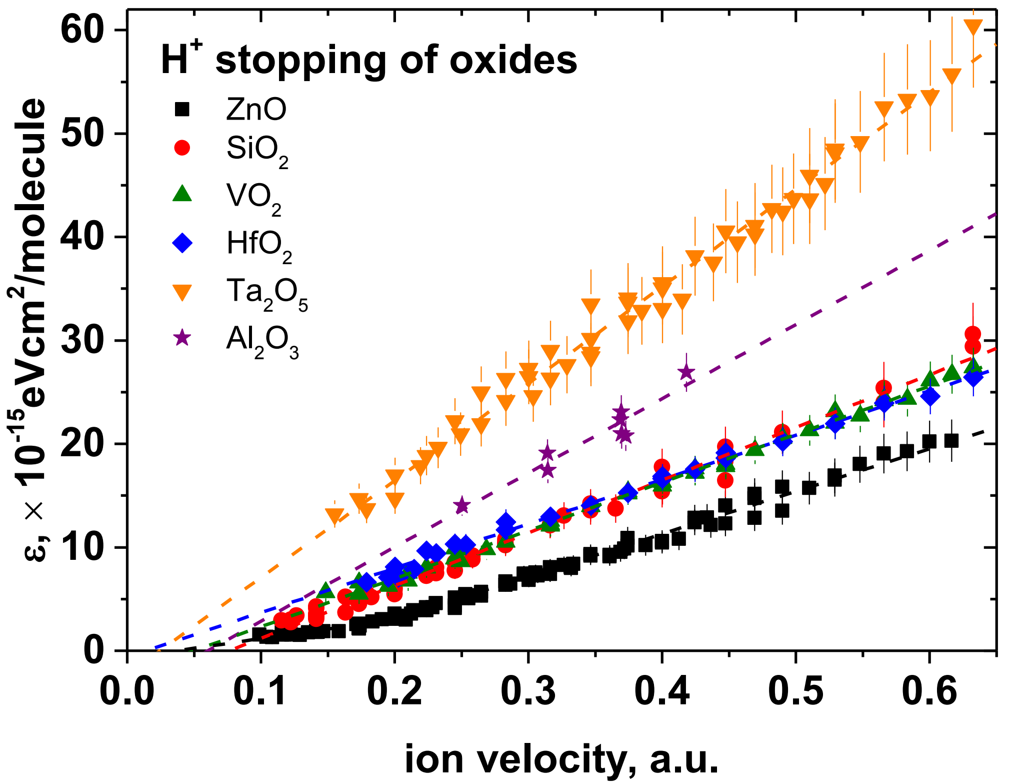
ELECTRONIC STOPPING OF H^+ IN OXIDES:
ε per molecule ↔ Free Electron Gas model?



SiO_2 data: S.N. Markin et al., PRL 103, 113201 (2009)
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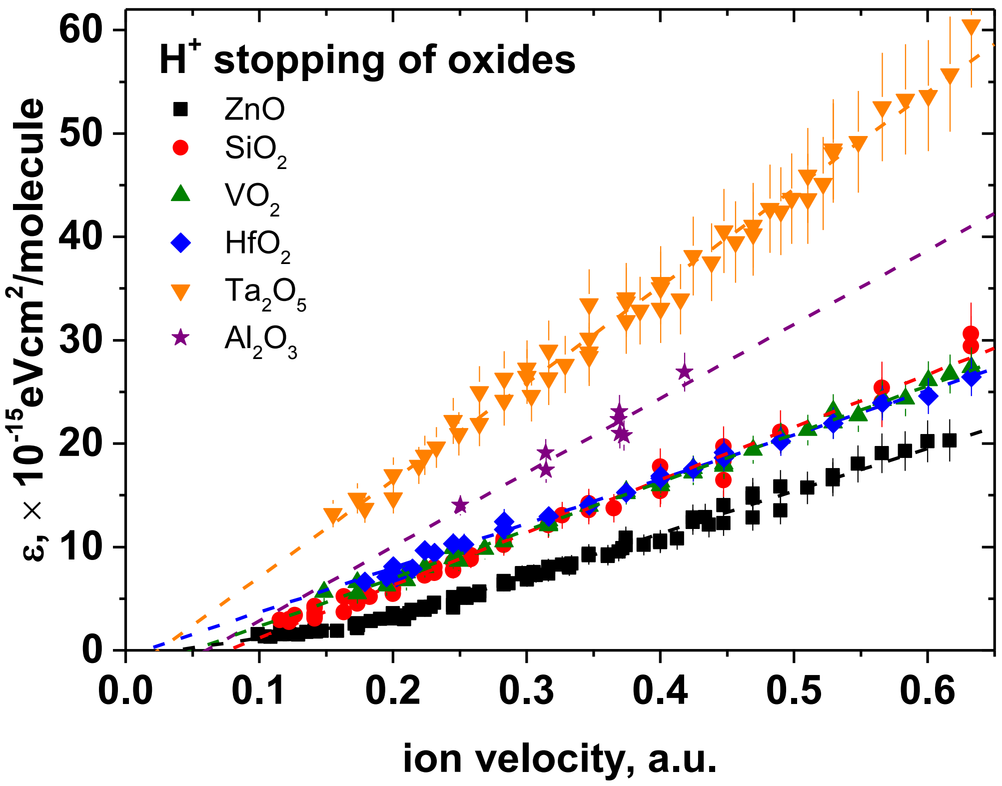
ELECTRONIC STOPPING OF H^+ IN OXIDES:
ε per molecule ↔ number of valence electrons?



SiO_2 data: S.N. Markin et al., PRL 103, 113201 (2009)
Al_2O_3 data: K. Eder et al., PRL 78, 4112-4115 (1997)

↔

	N_{val}
VO_2	13
ZnO	6
Ta_2O_5	30
HfO_2	12
Al_2O_3	18
SiO_2	12

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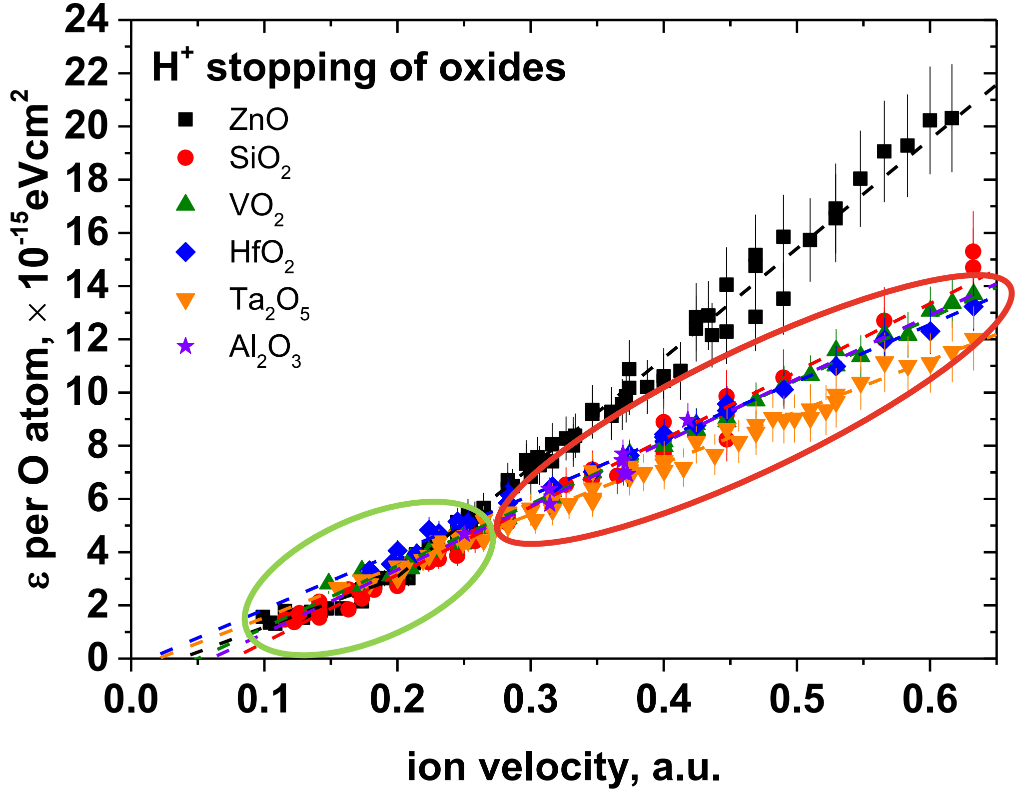
ELECTRONIC STOPPING OF H^+ IN OXIDES: ε per O atom



SiO_2 data: S.N. Markin et al., PRL 103, 113201 (2009)
Al_2O_3 data: K. Eder et al., PRL 78, 4112-4115 (1997)

- $v < 0.2$ a.u. (1 keV H^+): ε of all oxides coincide
- $v > 0.2$ a.u. (1 keV H^+): ε of most oxides group within 15 % exception: ZnO

Excitation of O 2*p* electrons?

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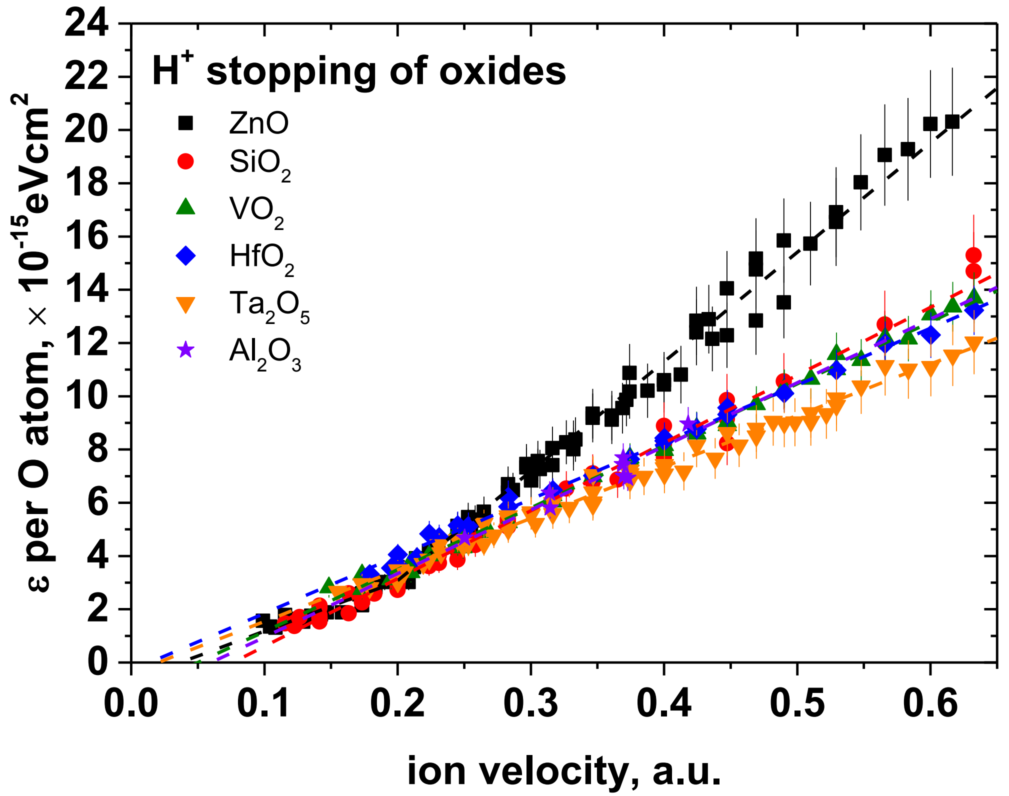
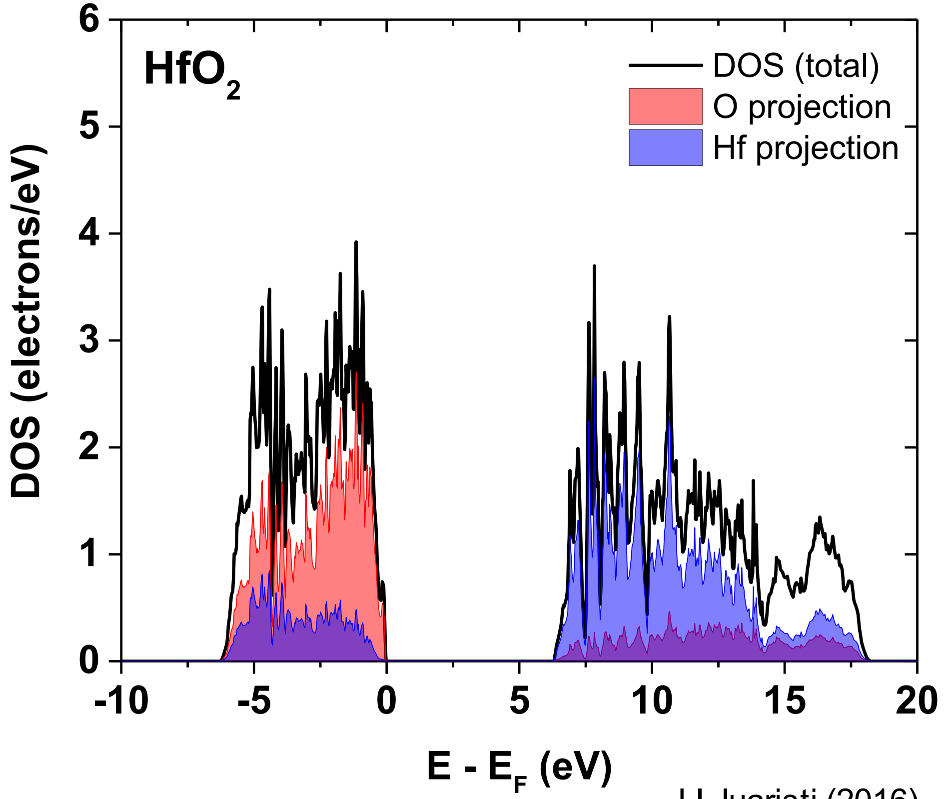
ELECTRONIC STOPPING OF H^+ IN OXIDES: example: HfO_2

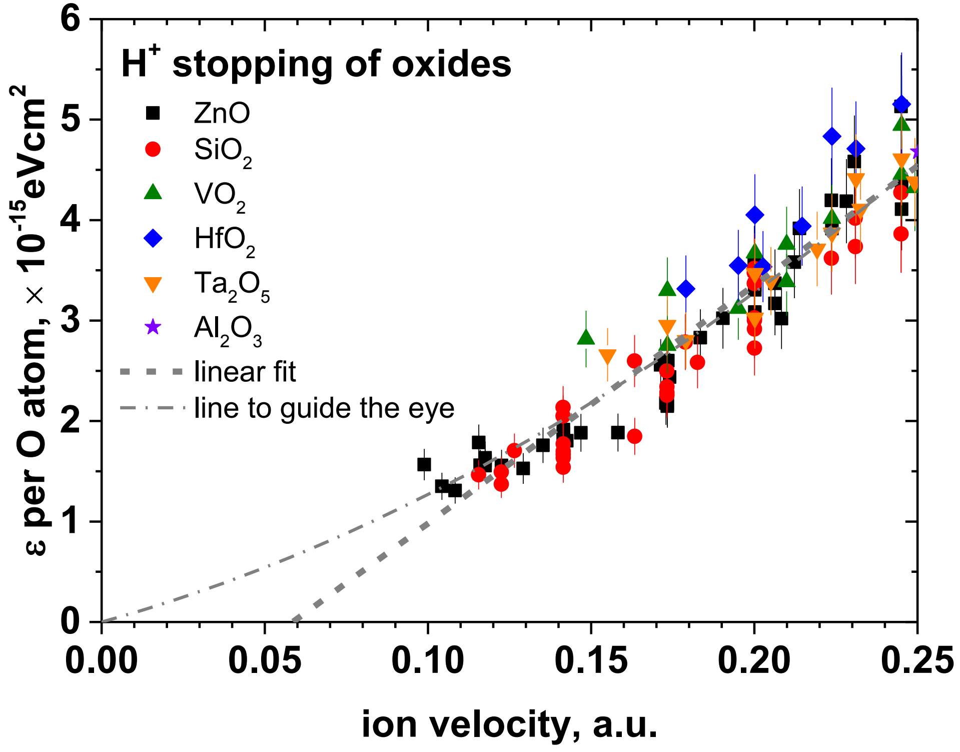




J.I. Iuaristi (2016)

Valence band of oxides is dominated by O 2*p* electrons

ELECTRONIC STOPPING OF H^+ IN OXIDES:
ε at low velocities ↔ # of O atoms



⟺

	E_{gap} (eV)	N_{val}	N_{val}/N_O
VO_2	0 … 0.7	13	6.5
ZnO	3.4	6	6
Ta_2O_5	4.5	30	6
HfO_2	5.5	12	6
Al_2O_3	8	18	6
SiO_2	9	12	6

$N_{val}/N_O \approx 6$ for all these oxides

N_O is decisive quantity for ε at $v << v_F$ – why?

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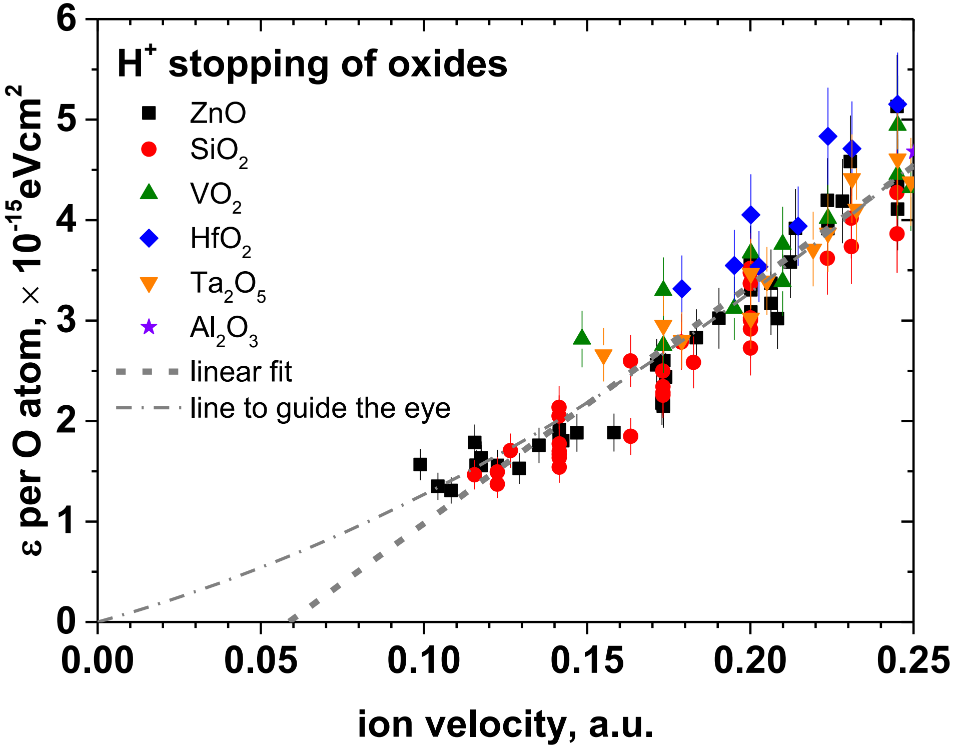
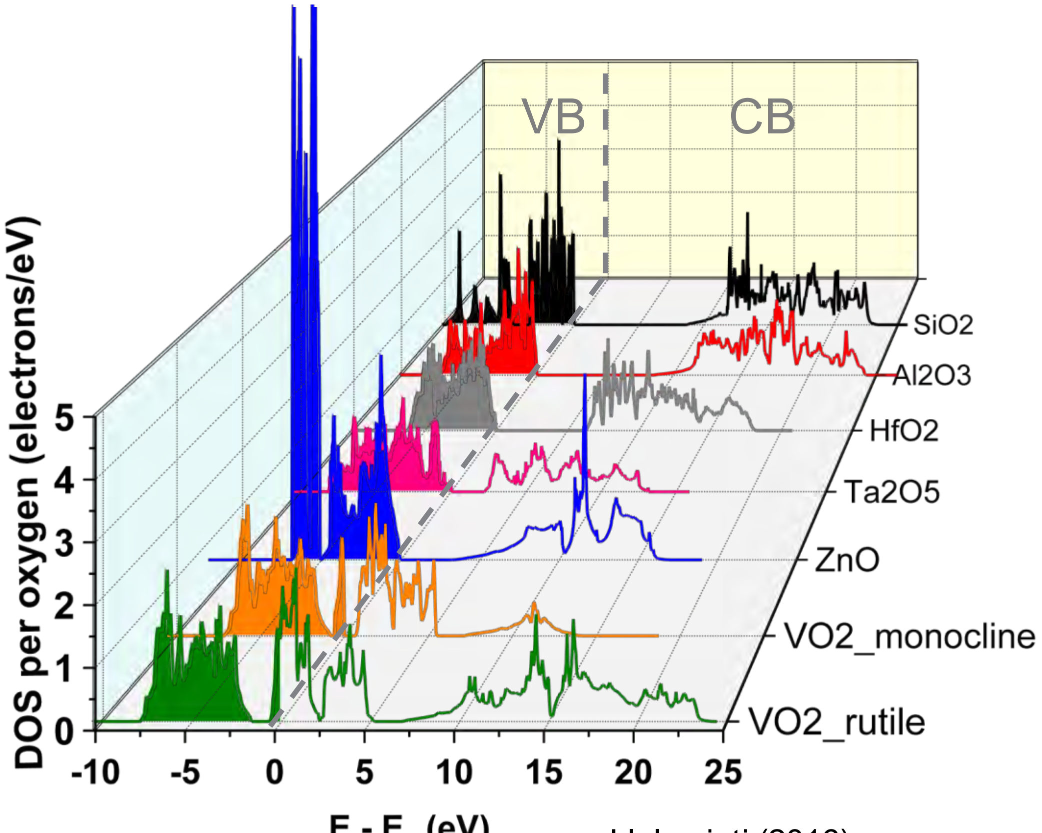
ELECTRONIC STOPPING OF H^+ IN OXIDES:
ε at low velocities ↔ DOS per O atom





Electronic stopping in oxides ↔ number of O atoms (similar N_{val} in VB)

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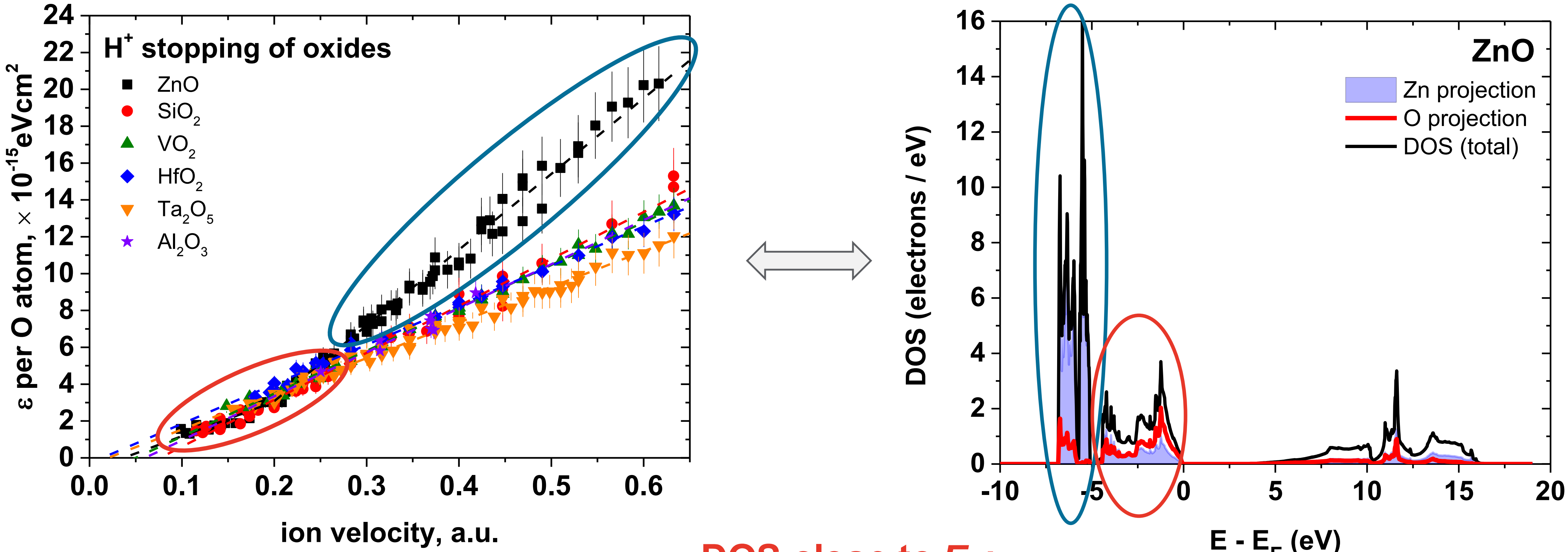
ELECTRONIC STOPPING OF H+ IN OXIDES: special case: ZnO

ZnO: *d*-band



DOS close to E_F:
mainly O electrons

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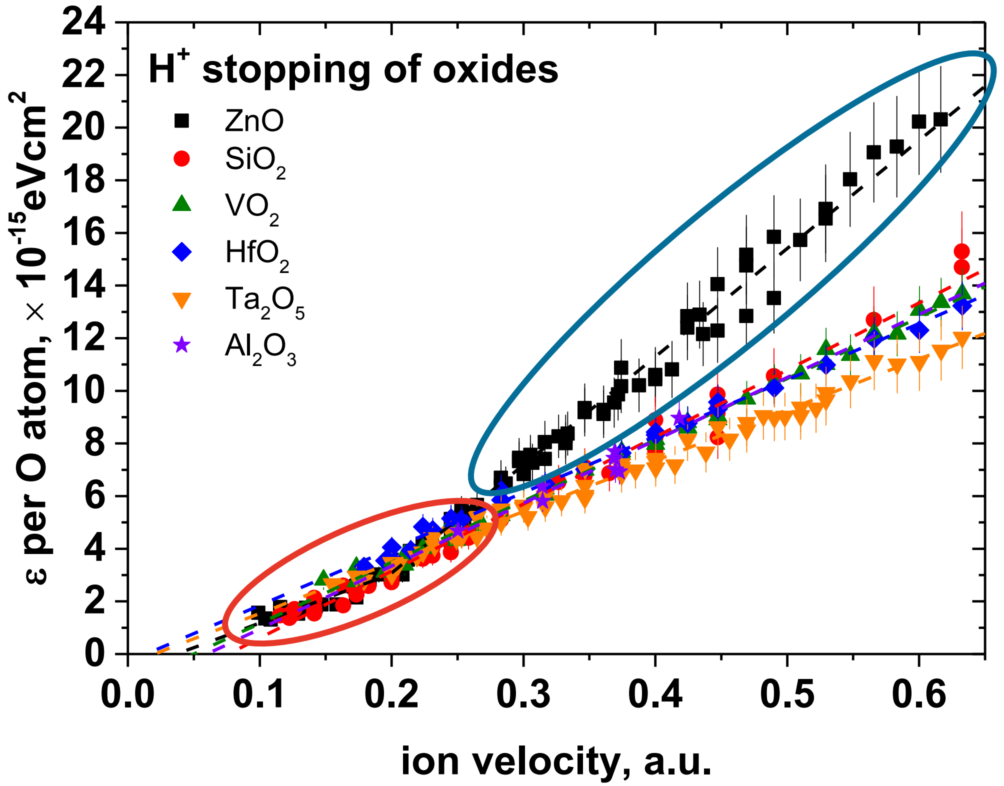
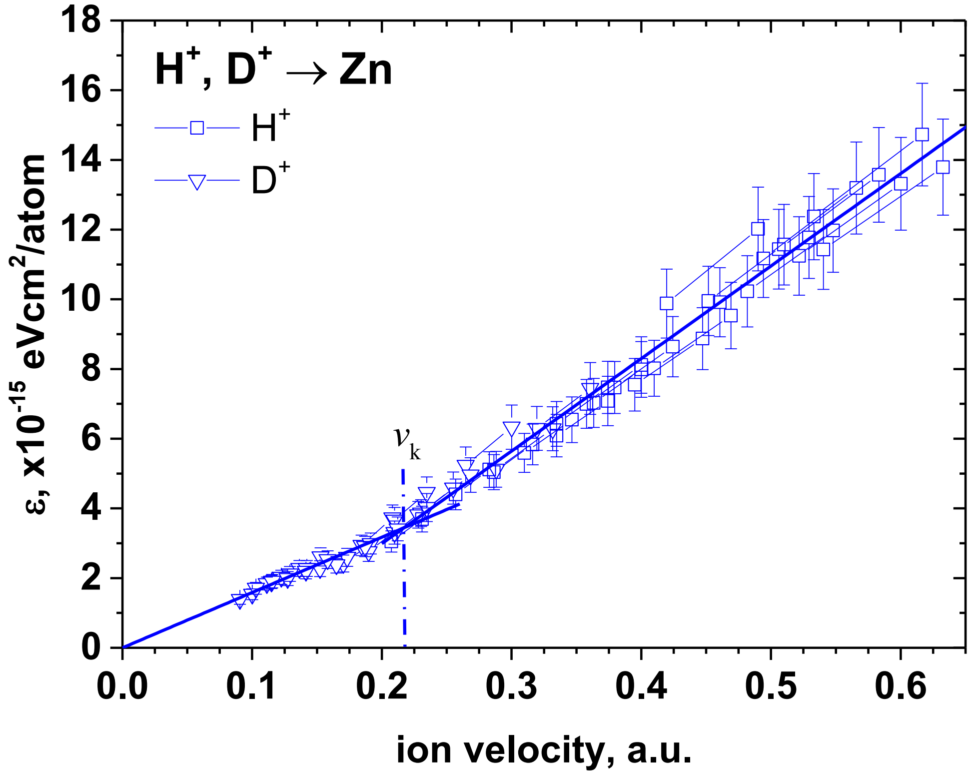
ELECTRONIC STOPPING OF H^+ IN OXIDES: special case: ZnO

“Kink” in ε also observed for Zn metal





D. Goebl et al., PRA 90, 042706 (2014)

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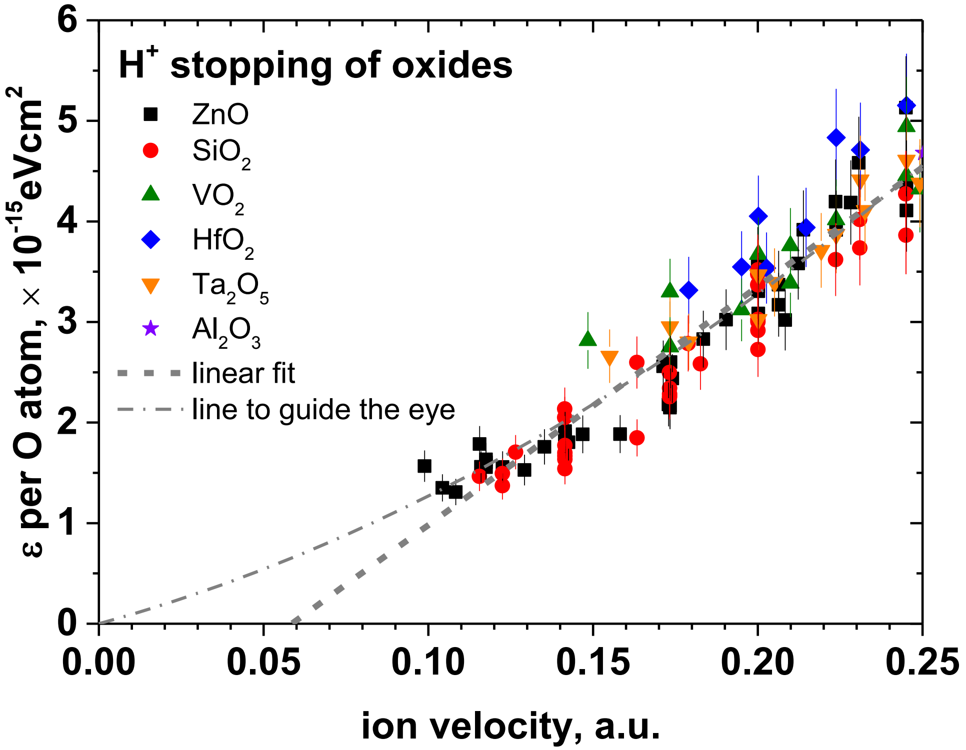
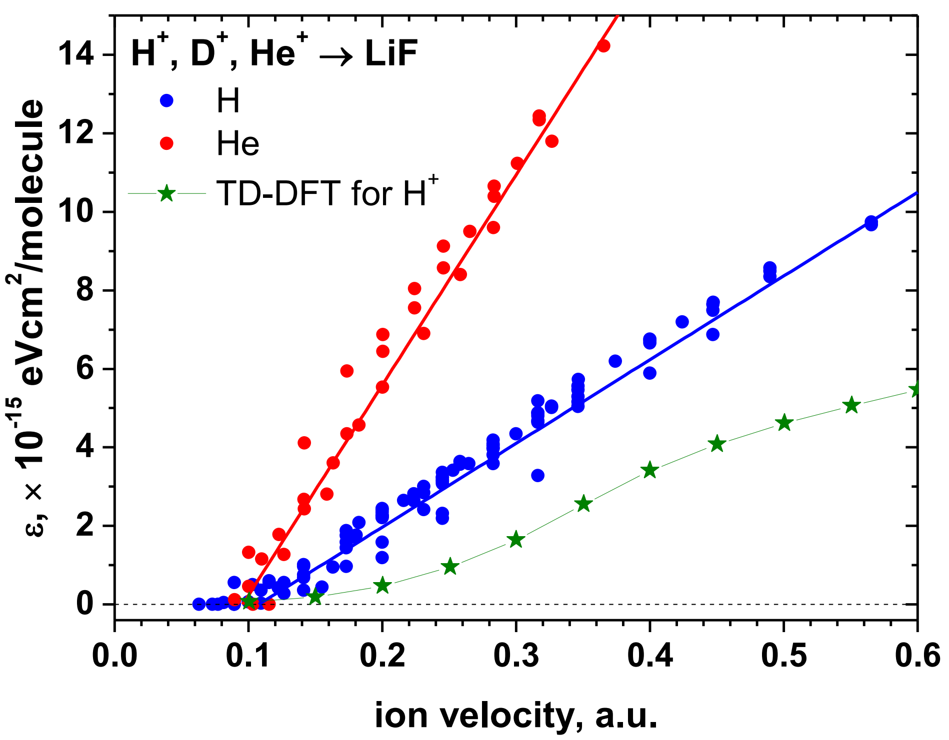
ELECTRONIC STOPPING OF H^+ IN OXIDES: velocity threshold?





apparent $v_{th} \approx 0.06$ a.u. for all these oxides ↔ independent of band gap

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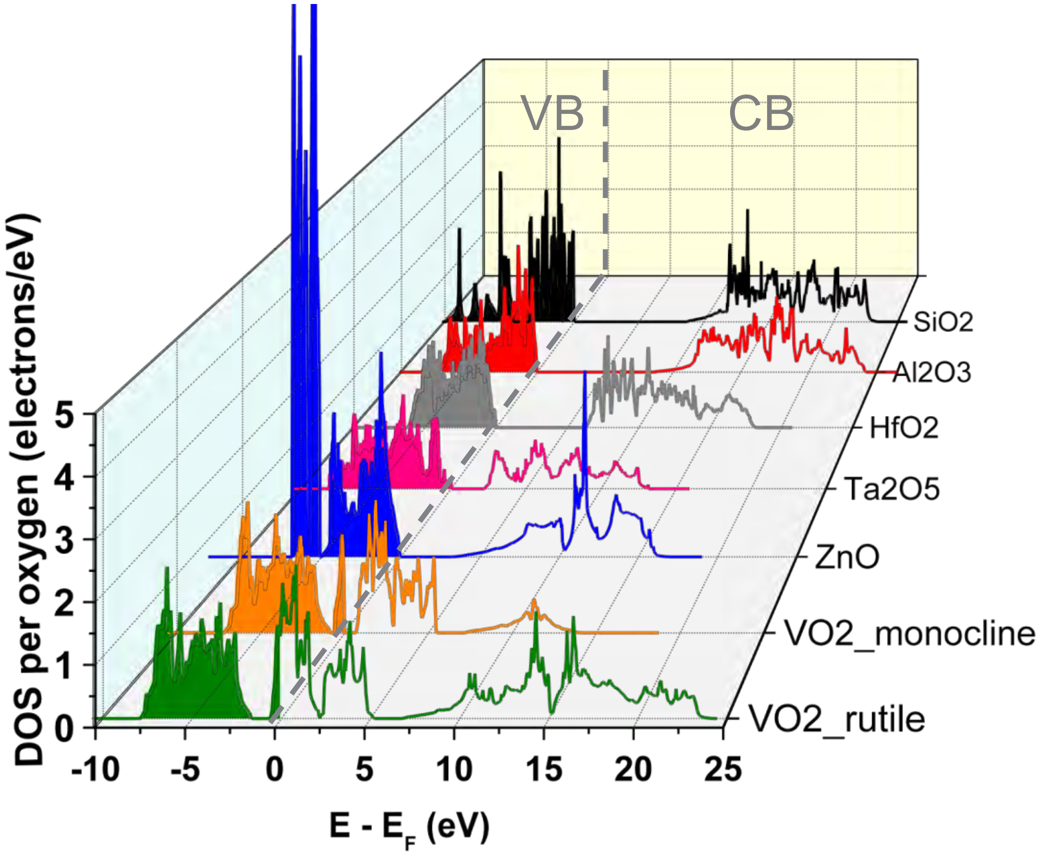
SUMMARY

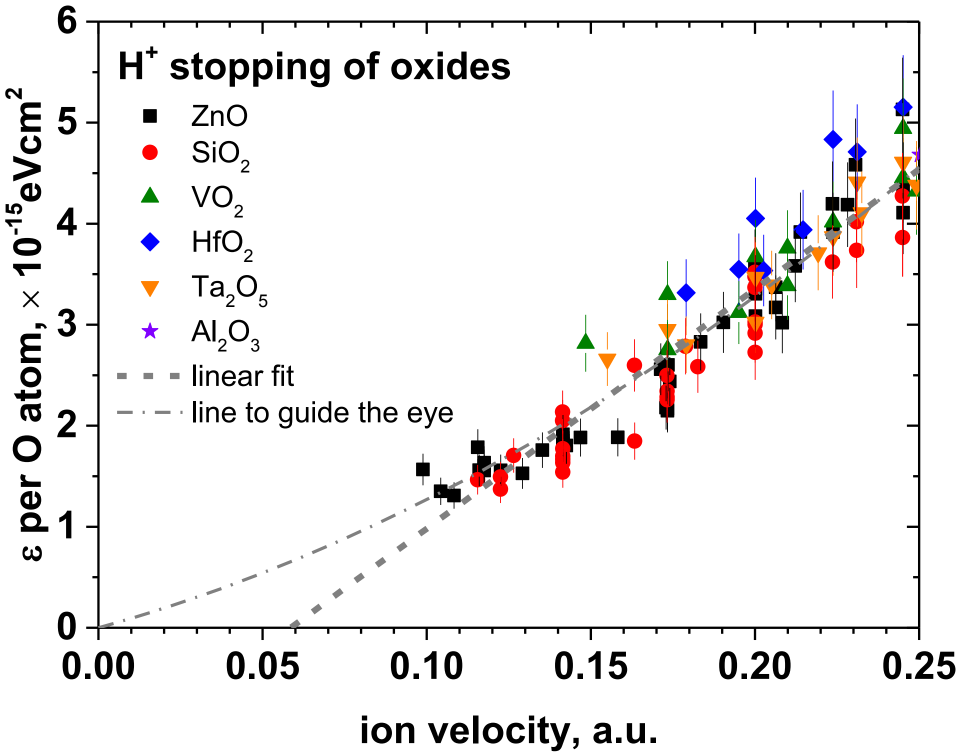
- H^+ in oxides: $\rightarrow N_{val}/N_O \approx 6$

  $\rightarrow$ DOS($E < E_F$) $\leftrightarrow$ # of O atoms

ε independent of band gap

unknown threshold behavior





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Daniel Primetzhofer

San Sebastián:
J. Iñaki Juaristi
Maite Alducin
Pedro M. Echenique
Andres Arnau
Daniel Sanchez Portal





FWF Der Wissenschaftsfonds.

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THANK YOU FOR YOUR ATTENTION!
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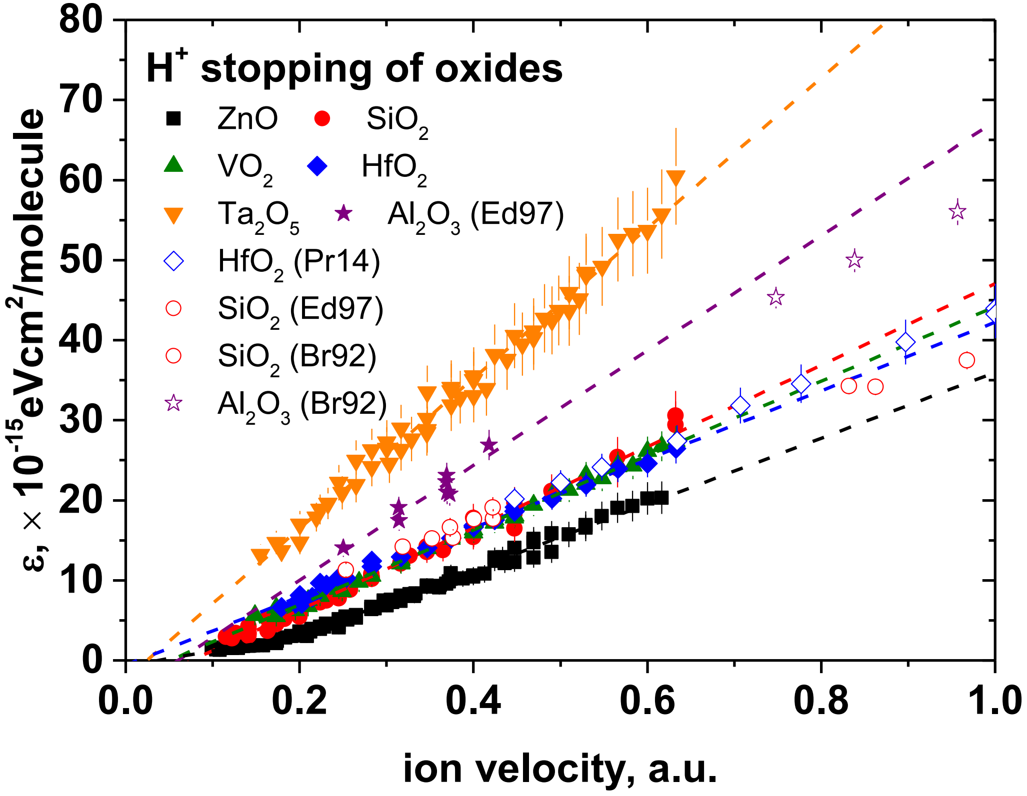
ELECTRONIC STOPPING OF H^+ IN OXIDES: ε per molecule – comparison with literature



- HfO_2: excellent agreement between LEIS and MEIS data from Uppsala
- SiO_2: excellent agreement between LEIS data, RBS data from Linz and data from Fritz Aumayr‘s group in Vienna
- Al_2O_3: very good agreement between RBS data from Linz and data from Vienna

SiO_2 data: S.N. Markin, D. Primetzhofer, P. Bauer, Phys. Rev. Lett 103, 113201 (2009)
Al_2O_3 data: K. Eder, D. Semrad, P. Bauer, R. Golser, P. Maier-Komor, F. Aumayr, M. Penalba, A. Arnau, J.M. Ugalde, P.M. Echenique, Phys. Rev. Lett. 78, 4112-4115 (1997)

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