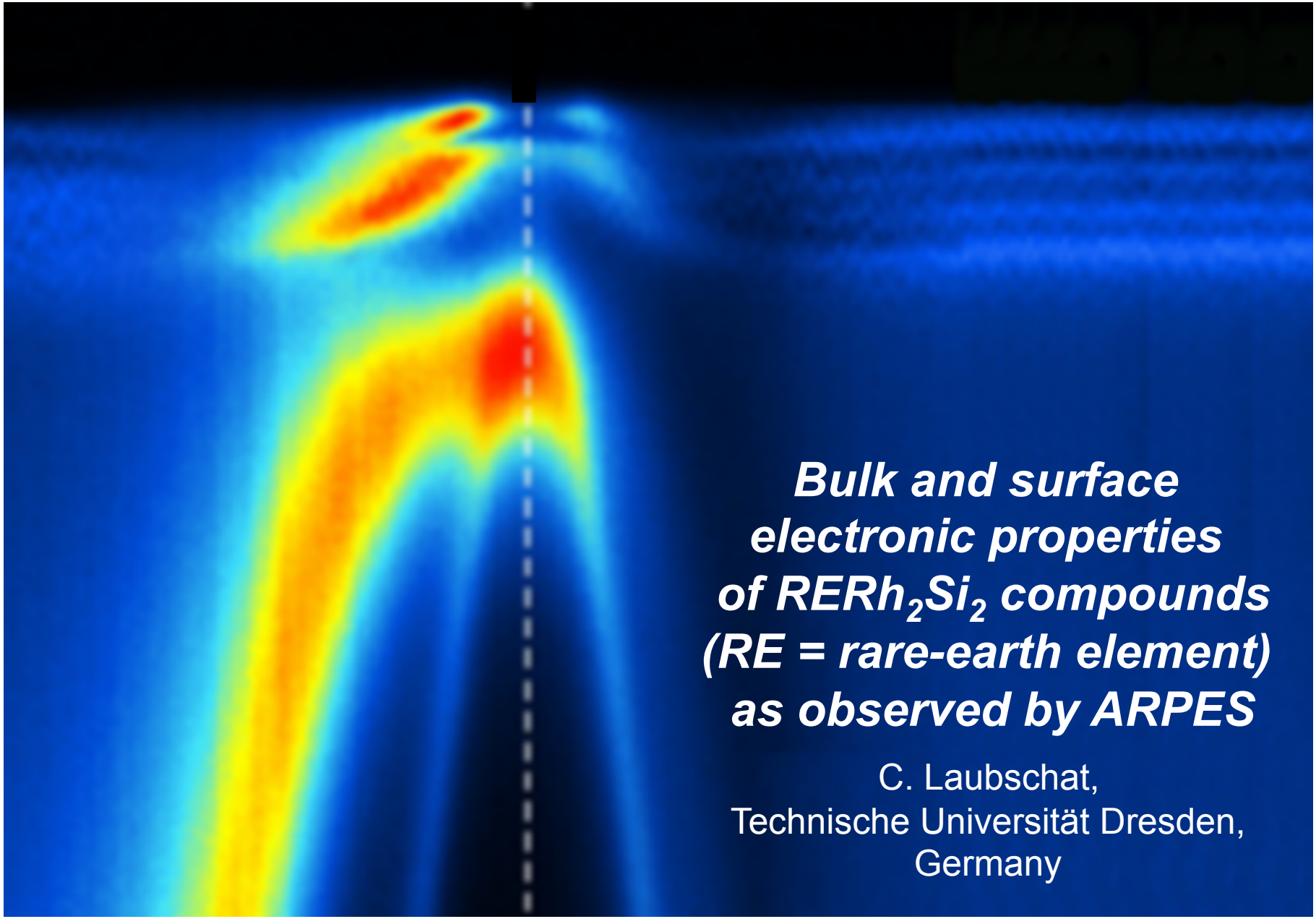

Bulk and surface electronic properties of $RERh_2Si_2$ compounds (RE = rare-earth element) as observed by ARPES

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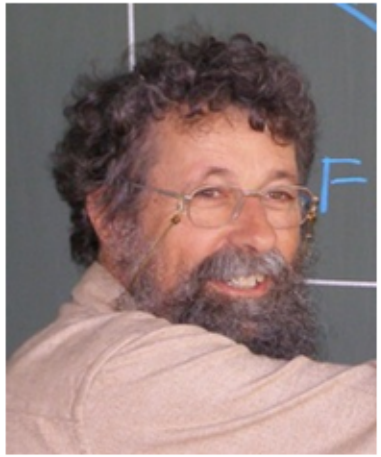

Christoph Geibel
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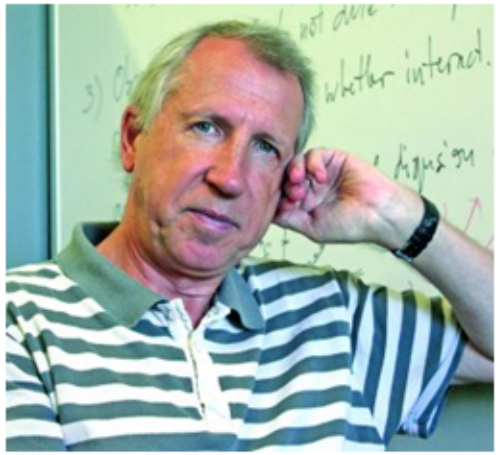
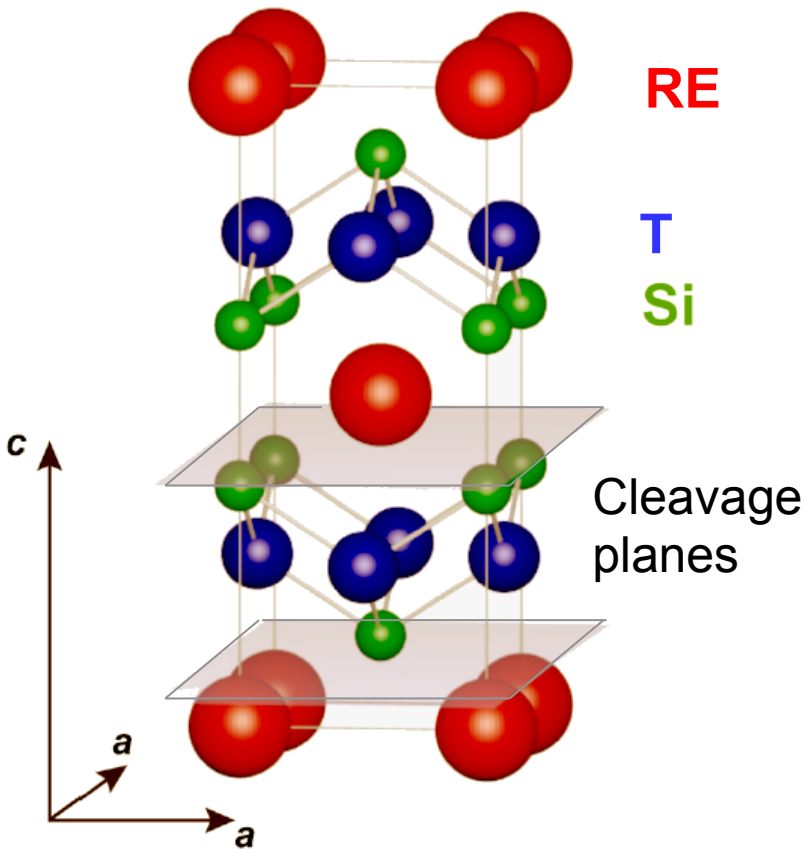
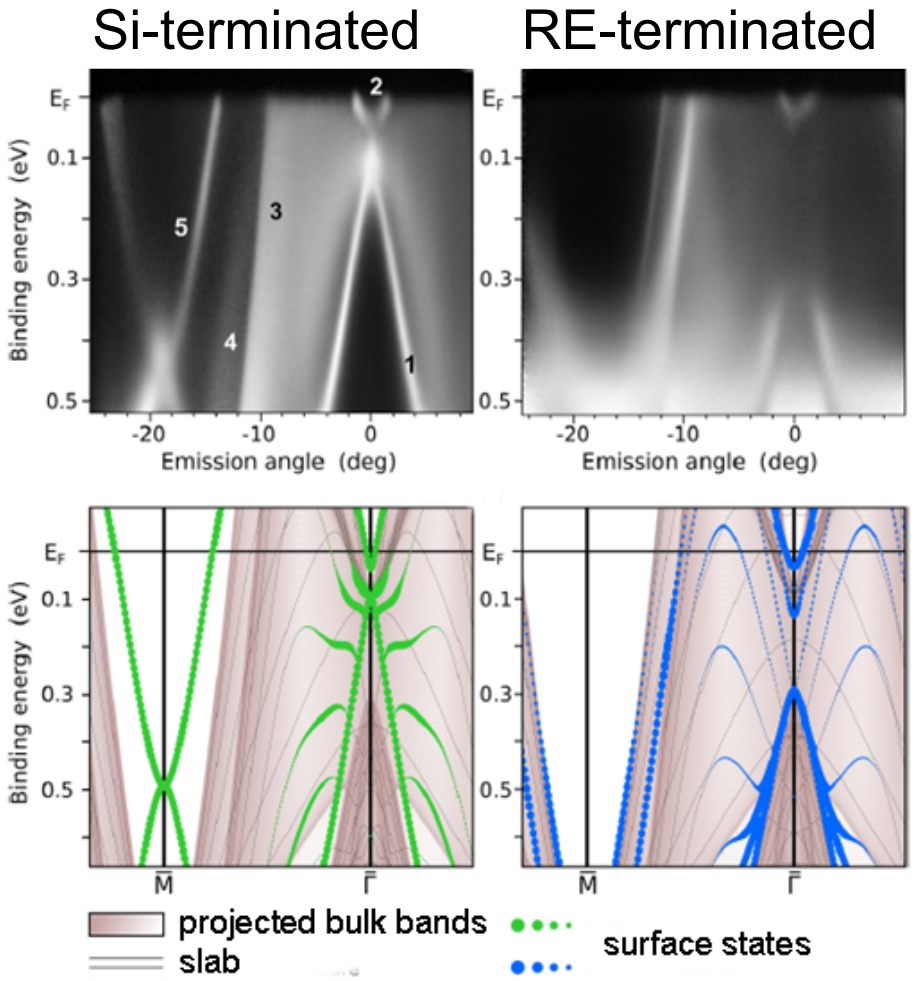
Frankfurt



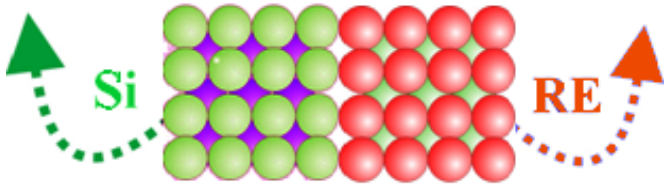
Eugeny Chulkov
San Sebastian

RET_2Si_2 compounds (RE = rare-earth, T = Co, Rh, Ir)



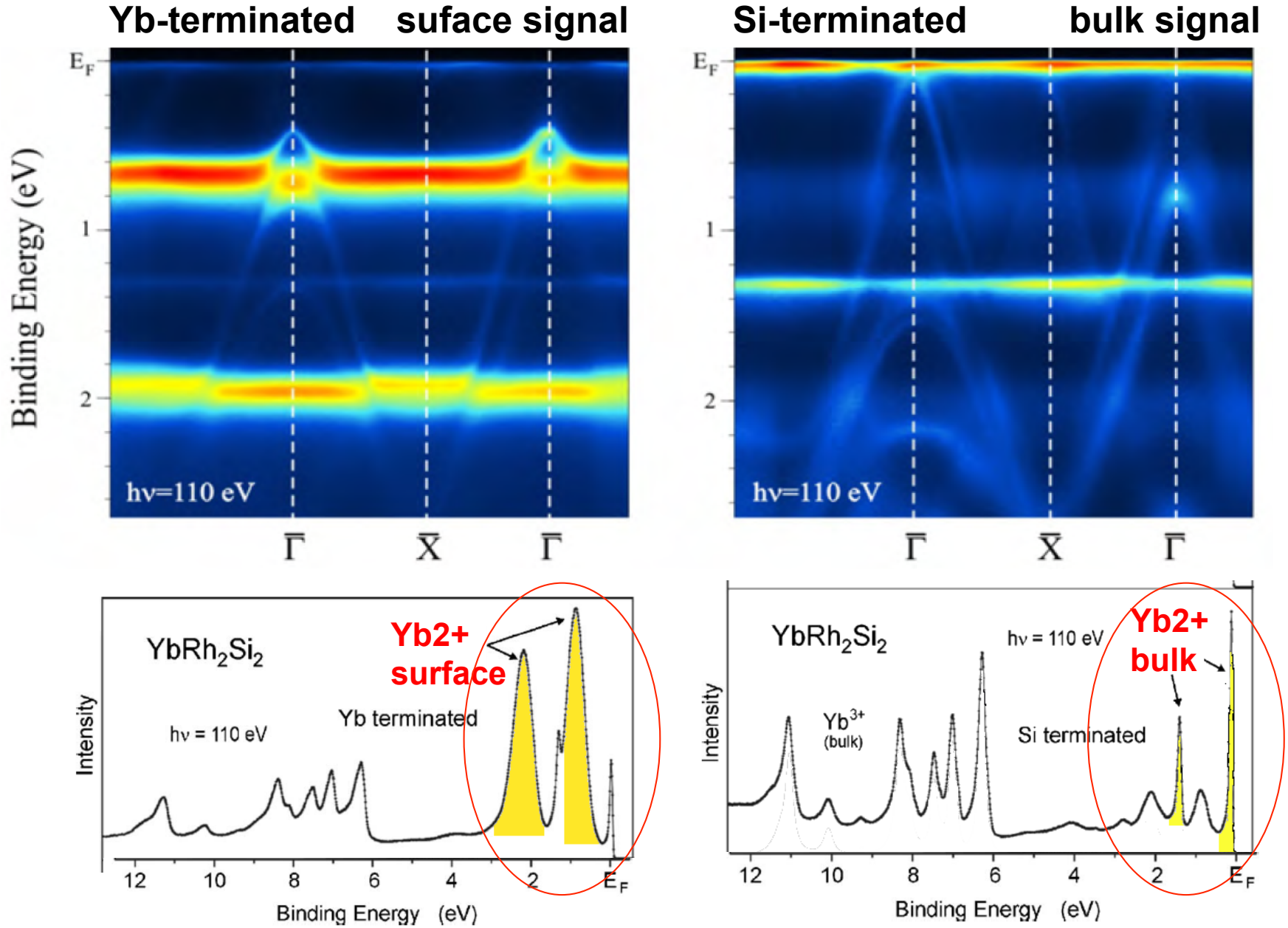


- $ThCr_2Si_2$-structure
- Tightly bond Si-T-Si blocks
  → cleavage between RE and Si layers
- Surface state at Si-terminated surfaces



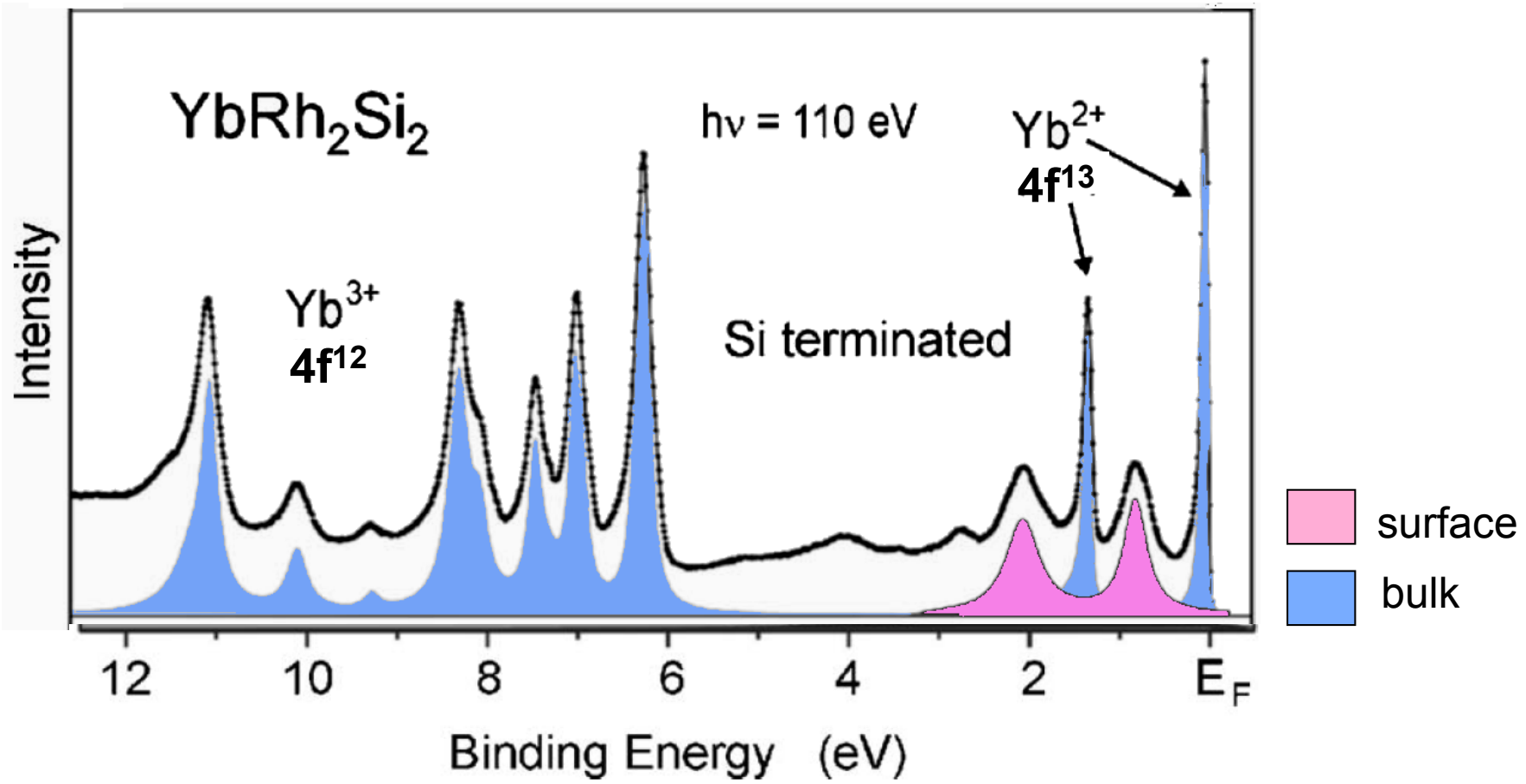
M. Güttler et al., PRB 90,195138 (2014)

$YbRh_2Si_2$, mean valence ~2,9



S. Danzenbächer et al., PRB 75, 45109 (2007)

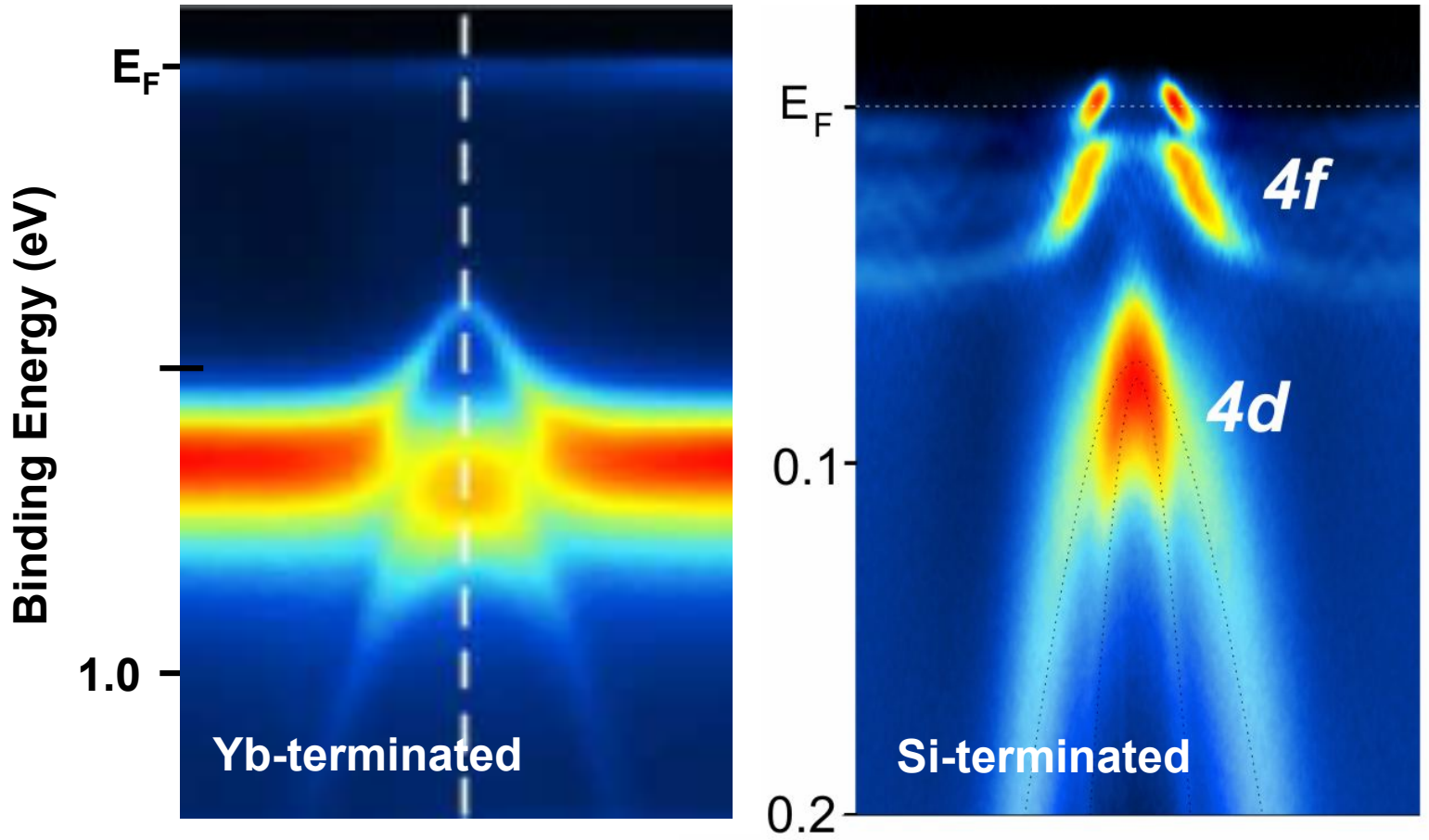
$YbRh_2Si_2$: Analysis within SIAM



- Bulk emission governed by stron $4f^{12}$ final-state multiplet and weak $4f^{13}$ doublet → mixed valent, valence 2,93

  SIAM-Parameter: Epsilon_*f* = 0.1 eV, Delta = 0.12 eV, U_{ff} = 6 eV
- Surface emission: Purely divalent

$YbRh_2Si_2$: Yb and Si-termination



- Induced 4f-dispersion due to “avoid crossing“ of Rh-4d-band
- Bulk: 4f crystal field splittings + 4f Fermi-level crossing → HF system
- Yb surface: No CEF splittings and Fermi-level crossings → stable Yb^{2+}

D.V. Vyalikh, PRL 105, 237601 (2010)

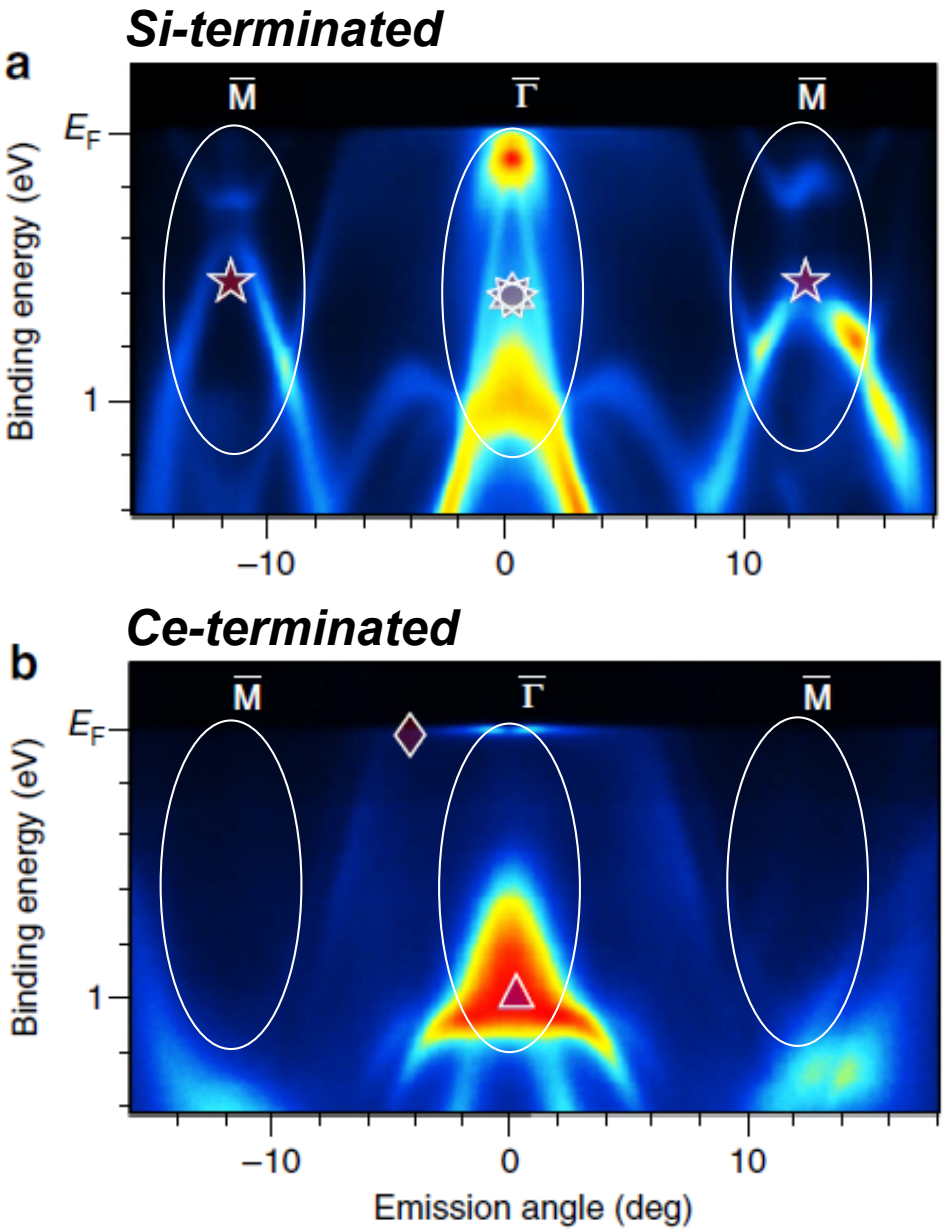
$CeRh_2Si_2$: Surface termination

- Surface termination may be determinated by watching the surface state within the large gap of the projected band-structure around the M-point (marked by star) which only exists at Si-terminated surfaces

- Also the surface resonance at the Γ-point (Dirac cone) is characteristic for Si-termination although there are underlying bulk bands weakly visible also at Ce termination.

- Data taken off-resonance at 112 eV photon energy

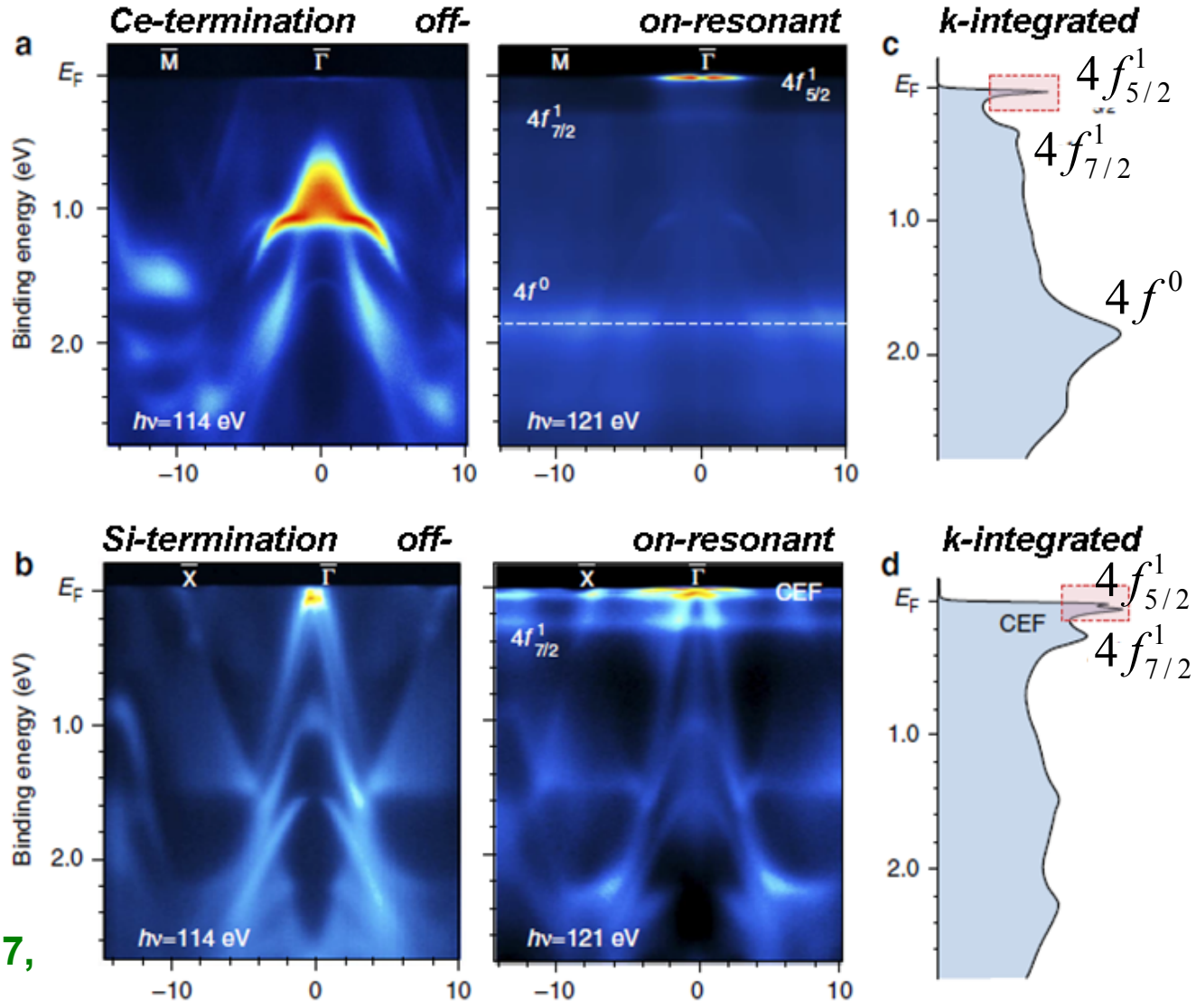
S. Patil et al., Nature Comm. 7, 11029 (2016)



$CeRh_2Si_2$: Bulk and surface electron structure

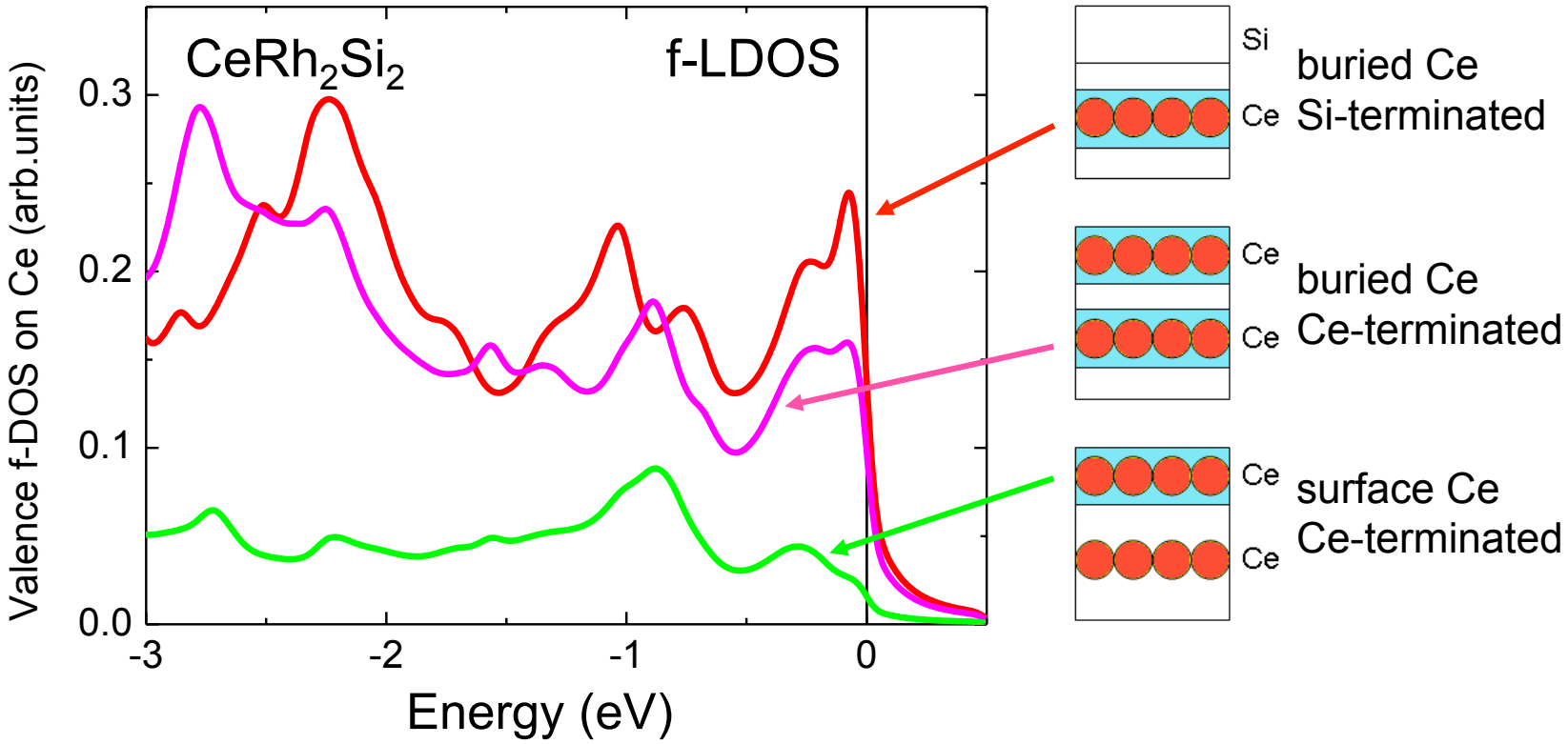
- **Ce at surface sites:**
  Well defined ionization peak ("$4f^0$"),
  $4f^1$ signal only around Γ-point consisting almost of $4f^1_{5/2}$ component at E_F..
  ⇒ **weakly hybridized**

- **Ce in the bulk:**
  $4f^0$-character fully merged into the valence band.
  Intense $4f^1_{5/2}$ emission with crystal field splitting and $4f^1_{7/2}$ side band.
  ⇒ **strongly hybridized**



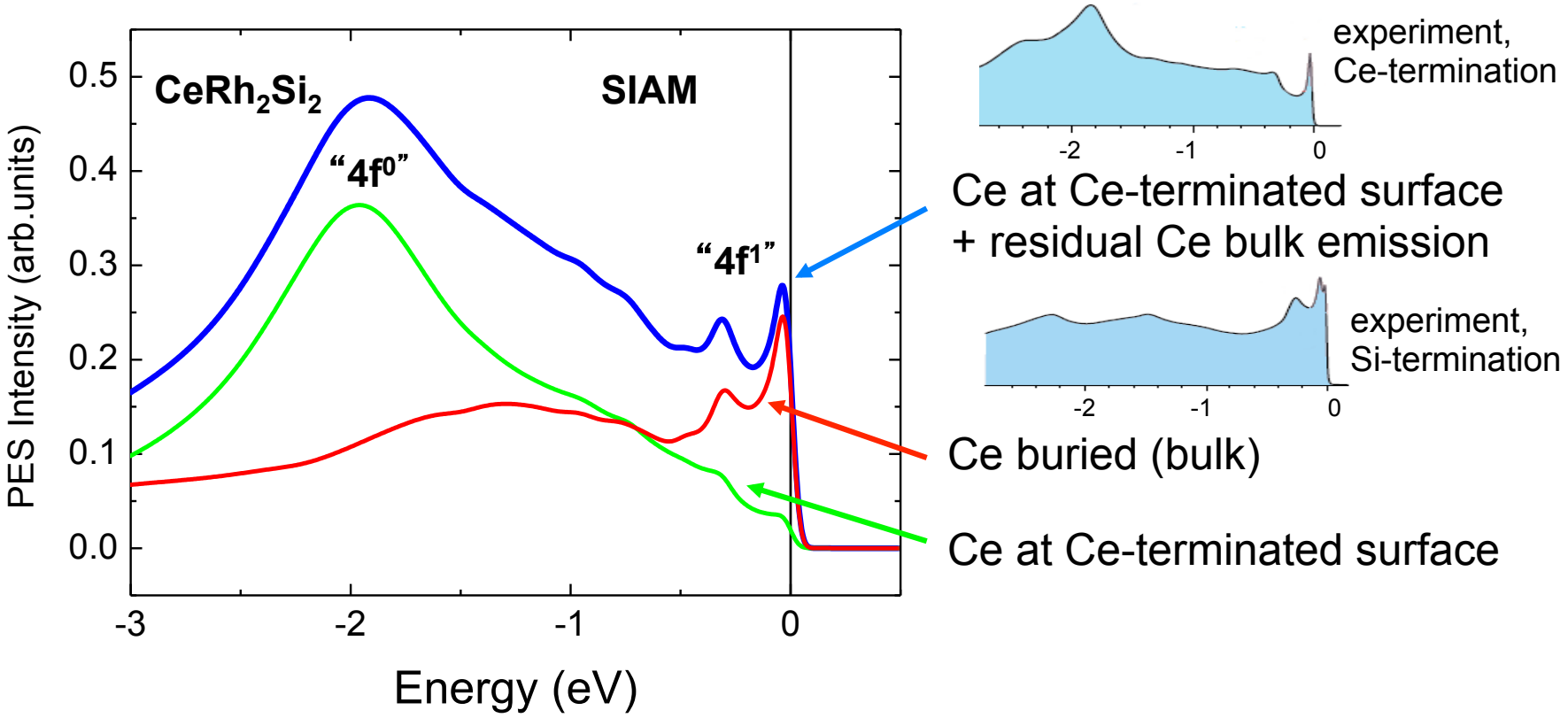
S. Patil et al., Nature Comm. 7, 11029 (2016)

Different hybridization in the bulk and at the surface



- hybridization ~ hopping probability 4f ↔ valence band f-LDOS
- surface: coordination reduced → hopping probability reduced
- surface: f-LDOS near E_F reduced → hopping probability reduced
- bulk: f-LDOS large around 2 eV → strong hybridization of $4f^0$-state

Simulation within the Single-Impurity Anderson-Model



Parameter: Bulk: Epsilon_*f* = - 1.7 eV, Delta = 1.05 eV, U_{ff} = 6 eV.
Surface: Epsilon_*f* = - 1.9 eV, Delta = 0.7 eV (70% from bulk),

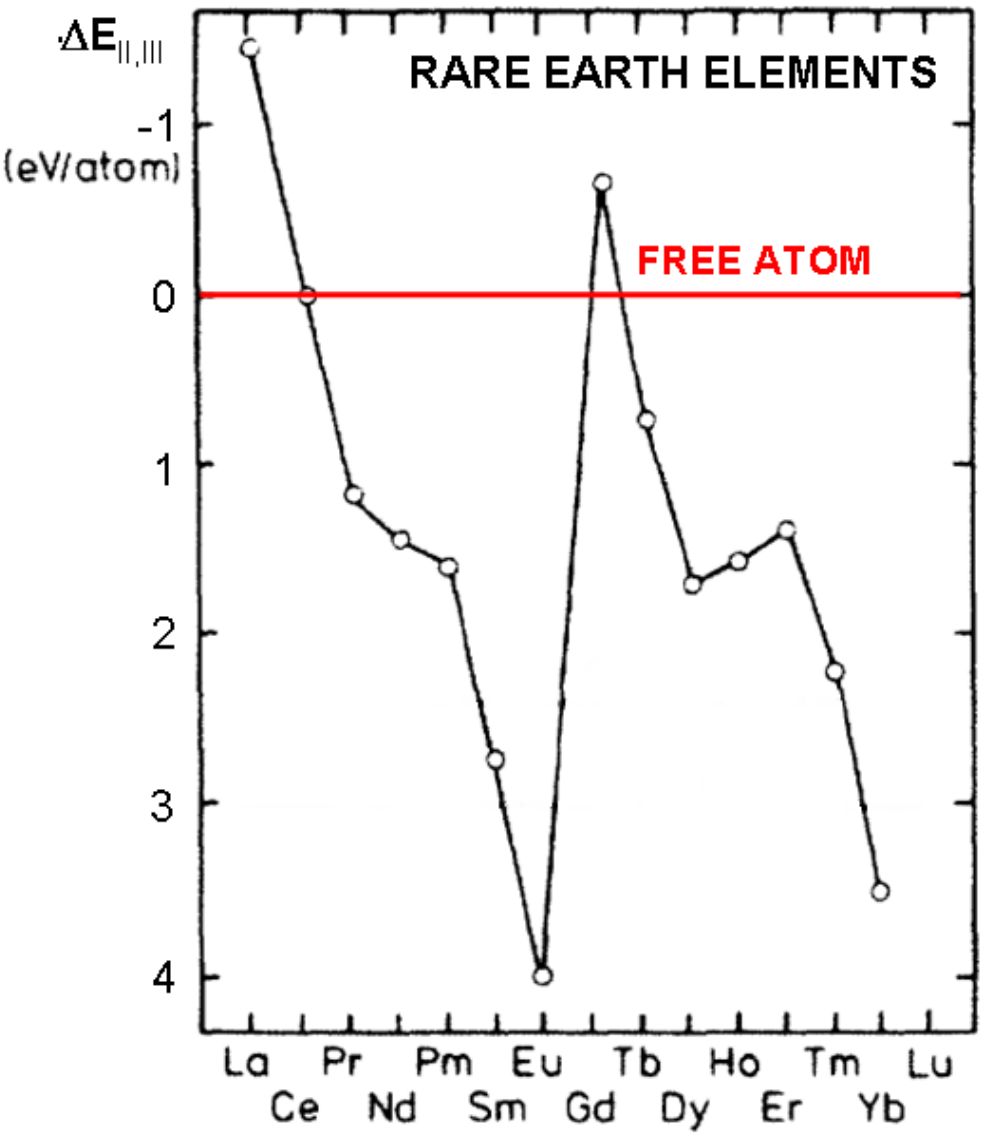
→ strong "$4f^1$"-signal for bulk Ce, shift and smearing of weak "$4f^{"0}$" component
→ weak"$4f^1$"-signal for Ce at surface, well pronounced "$4f^{"0}$" component

Thermochemical model: Valence of rare-earth elements

$\Delta E_{II,III}$: free atom excitation energy

$[Xe]4f^{n}(5d6s)^{2} \rightarrow [Xe]4f^{n-1}(5d6s)^{3}$

$\Rightarrow$ all rare-earths except La, Gd, Lu are divalent in the gas phase



B. Johansson, Phys. Rev. B20, 1315 (1979)

Valence of rare-earth elements

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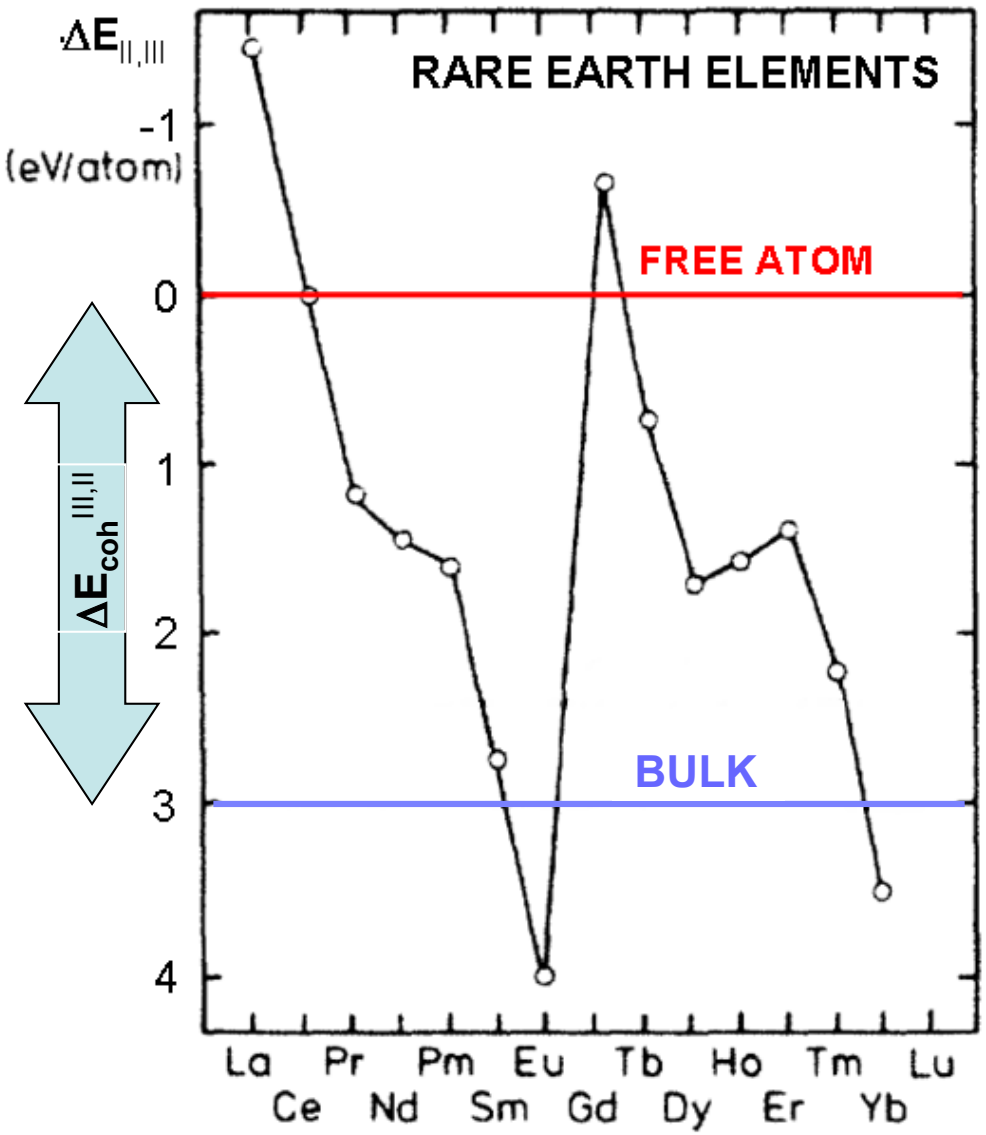
Metals: Gain in cohesive energy

$\Delta E_{coh}^{II,III} = E_{coh}^{III} - E_{coh}^{II}$

$\Rightarrow$ "zero line" shifts downwards

$\Rightarrow$ only Eu, Yb remain divalent



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Valence of rare-earth elements

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$\Delta E_{coh}^{II,III} = E_{coh}^{III} - E_{coh}^{II}$

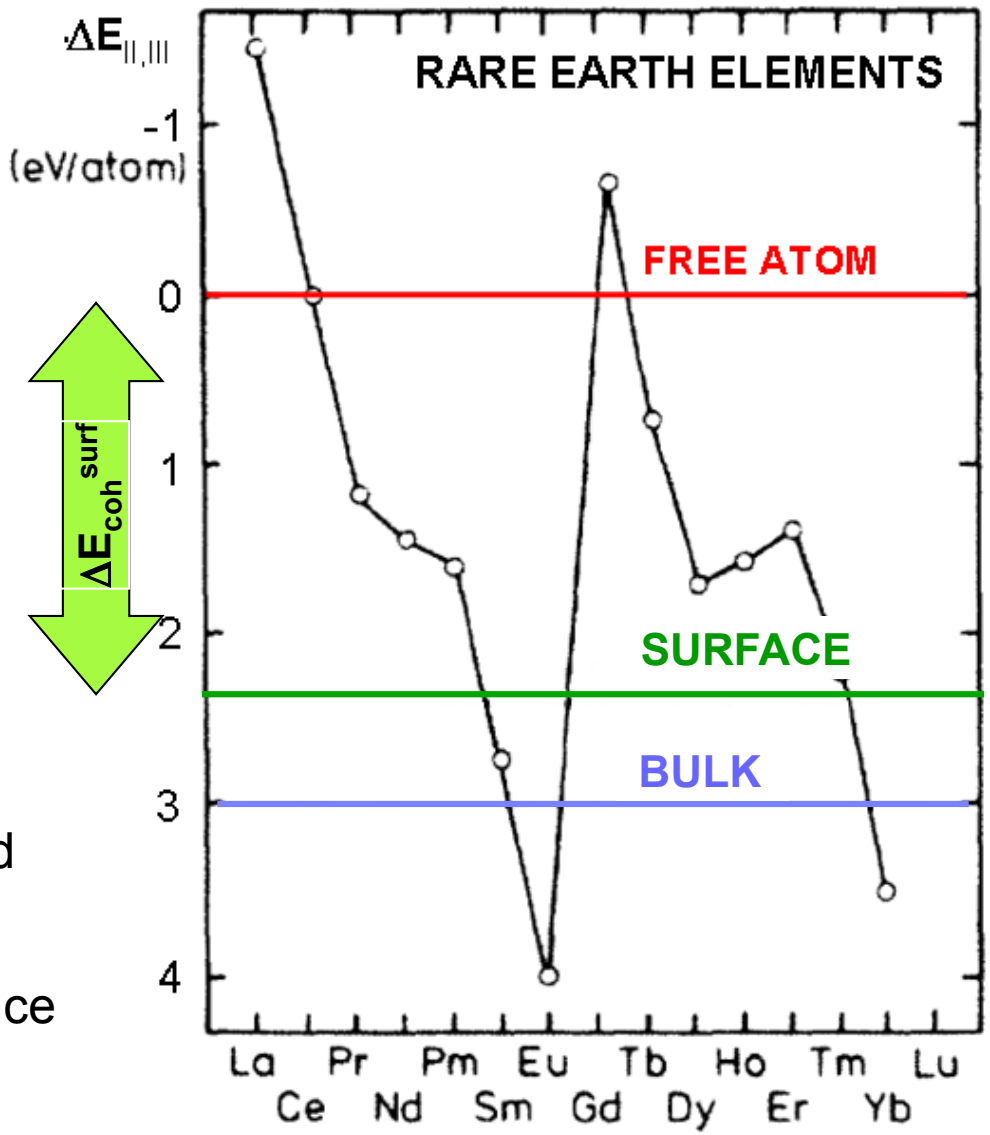
⇒ "zero line" shifts downwards

⇒ only Eu, Yb remain divalent

Surfaces: Cohesive Energy reduced

$\Delta E_{coh}^{surf} \approx 0{,}8 * \Delta E_{coh}^{bulk}$

⇒ Sm-metal reveals "surface valence transition" to divalent state



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Photoemission of 4f-states

Divalent systems:

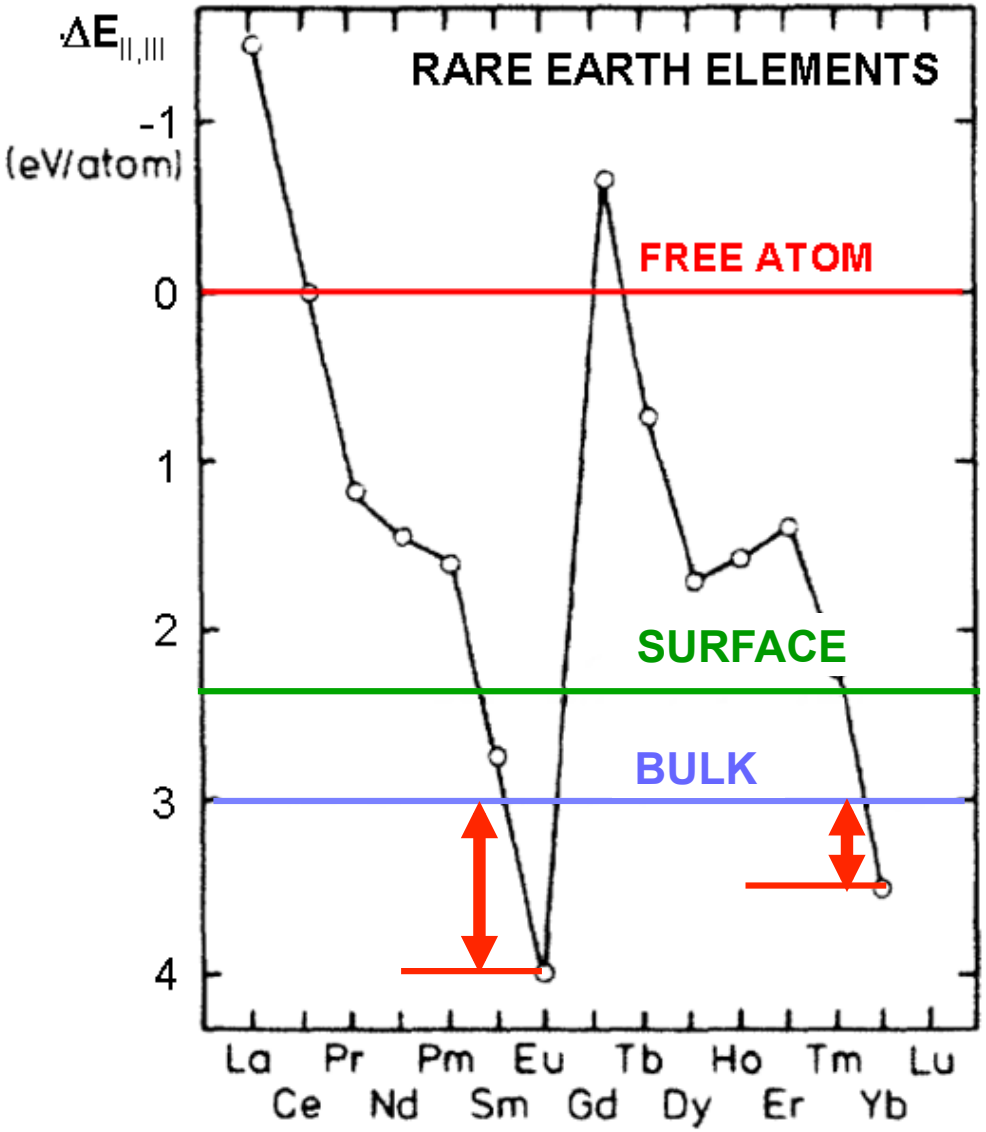
Fully screened final state

$E_{BIN} = \Delta E_{II,III} + E_{IMP}$

"Impurity term" considers that not the whole system undergoes valence transition

pure metals: $E_{IMP} \approx 0.6$ eV

compounds: $E_{IMP} \approx 0,1$ eV



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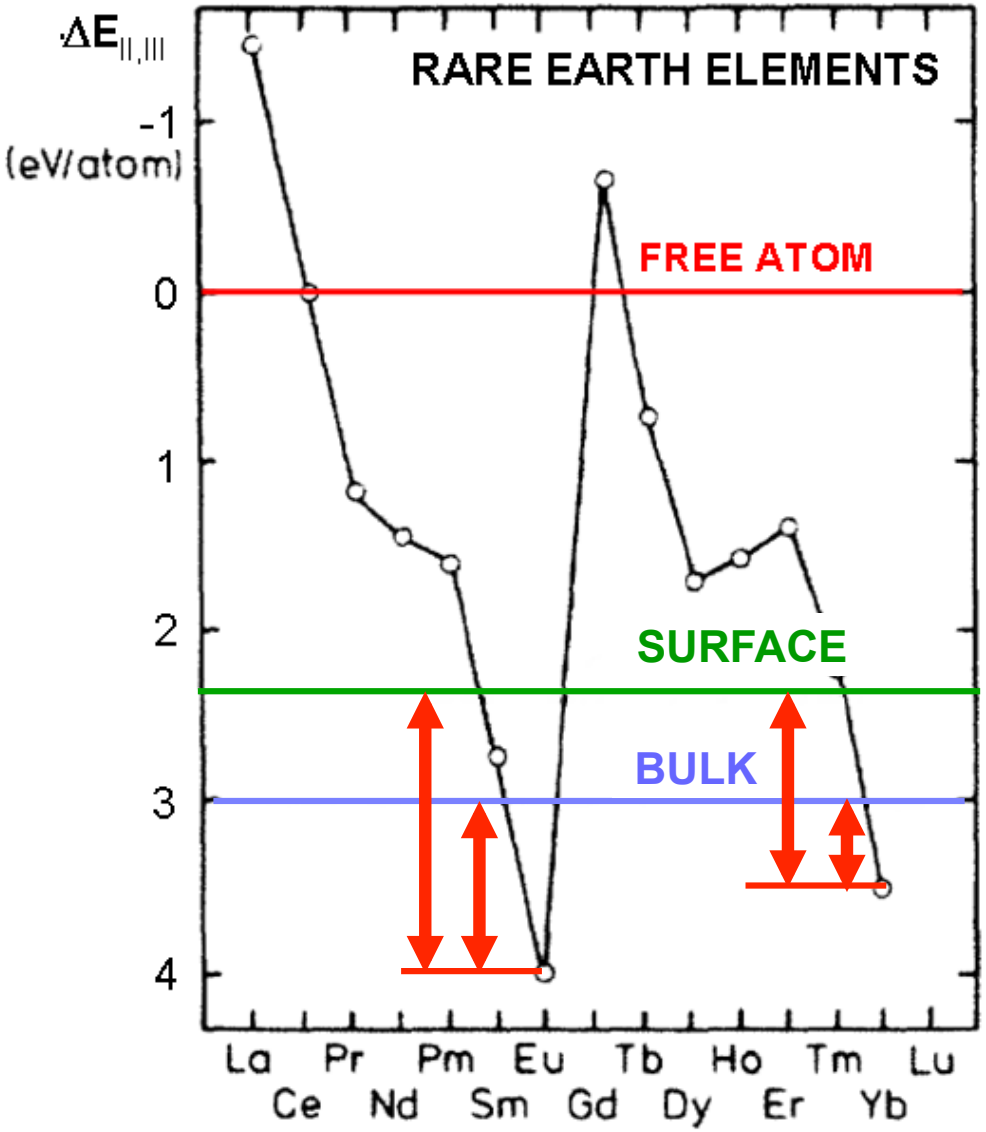
compounds: $E_{IMP} \approx 0{,}1$ eV

At surfaces E_{BIN} larger:

"surface core-level shift"



B. Johansson, Phys. Rev. B20, 1315 (1979)

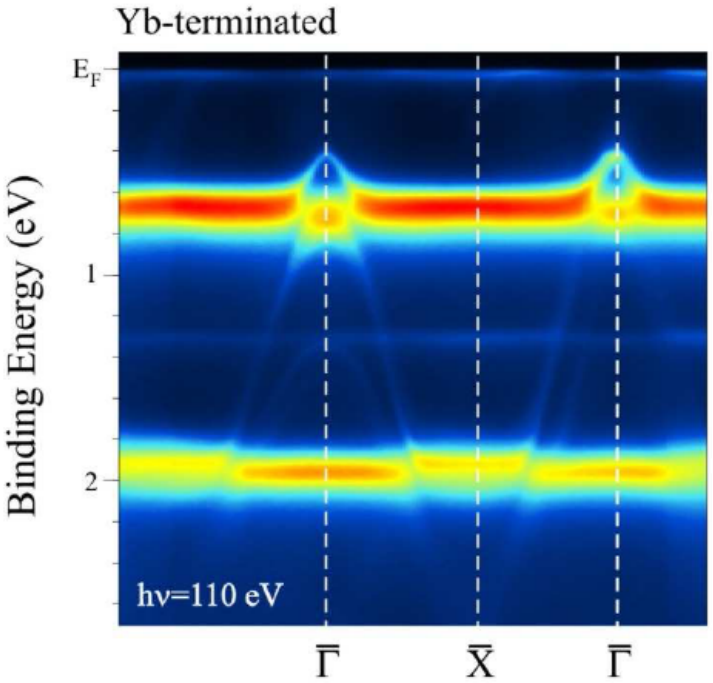
Photoemission of 4f-states

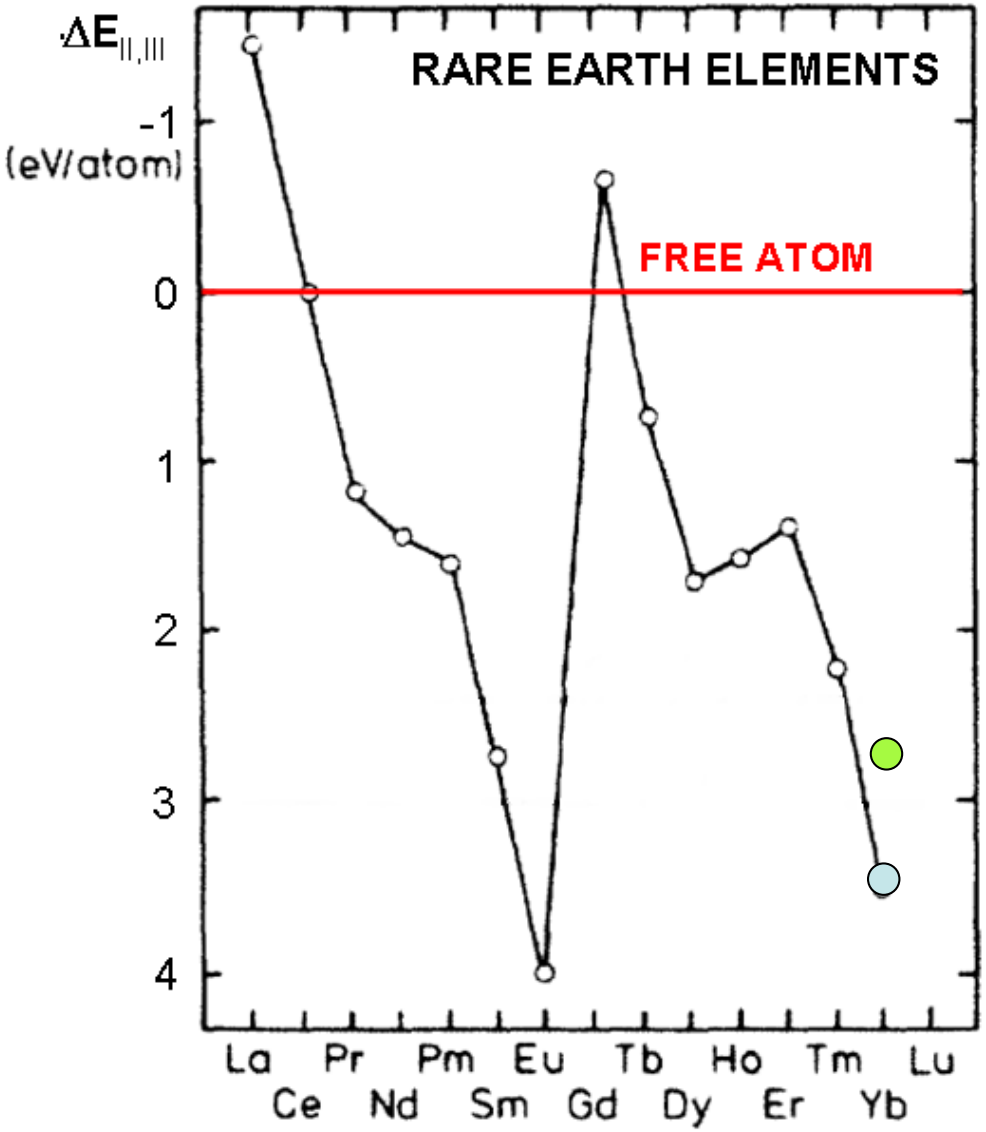
$RERh_2Si_2$ compounds:

RE = Yb: mixed-valent

E_{BIN} ≈ 0 eV,

E_{BIN}^{surf} ≈ 0,7 eV





Photoemission of 4f-states

$RERh_2Si_2$ compounds:

RE = Yb: mixed-valent

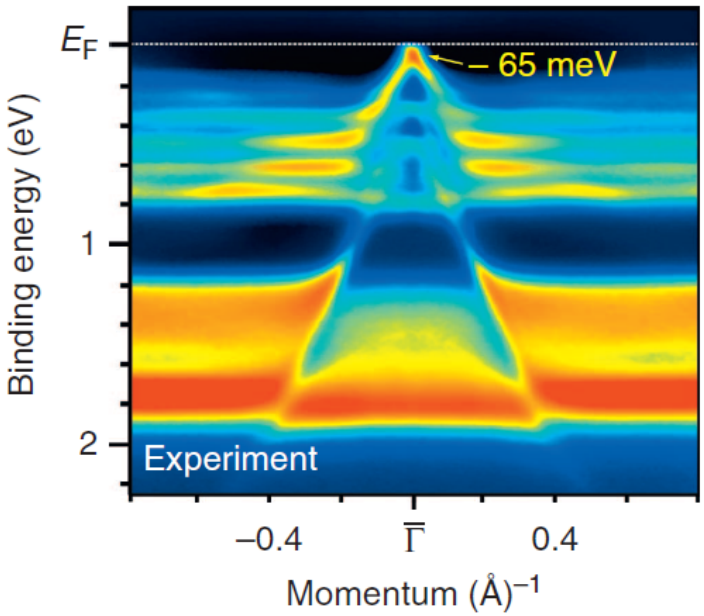
E_{BIN} ≈ 0 eV,

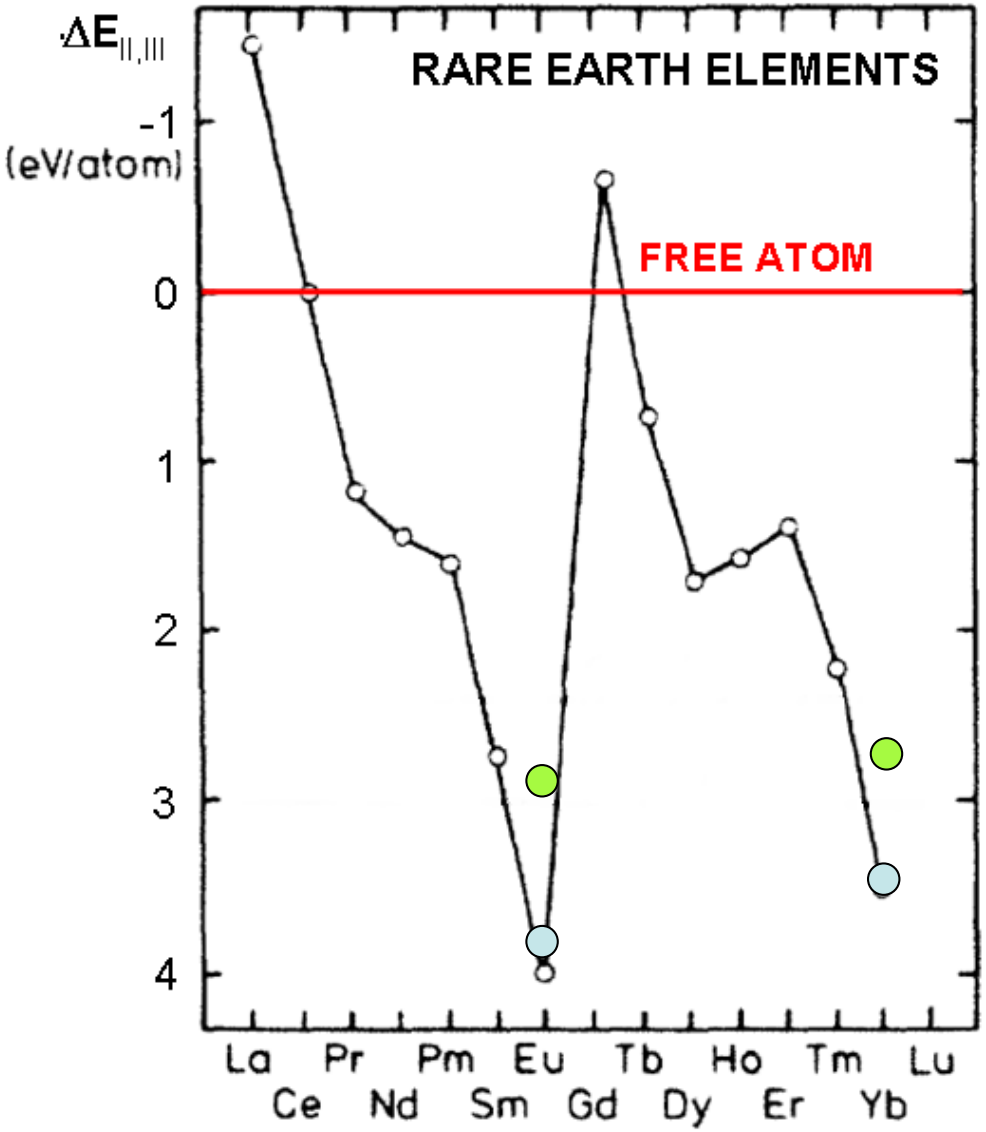
E_{BIN}^{surf} ≈ 0,7 eV

RE = Eu: divalent

E_{BIN} ≈ 0,2 eV,

E_{BIN}^{surf} ≈ 1,0 eV





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RE = Yb: mixed-valent

E_{BIN} ≈ 0 eV,

E_{BIN}^{surf} ≈ 0,7 eV

RE = Eu: divalent

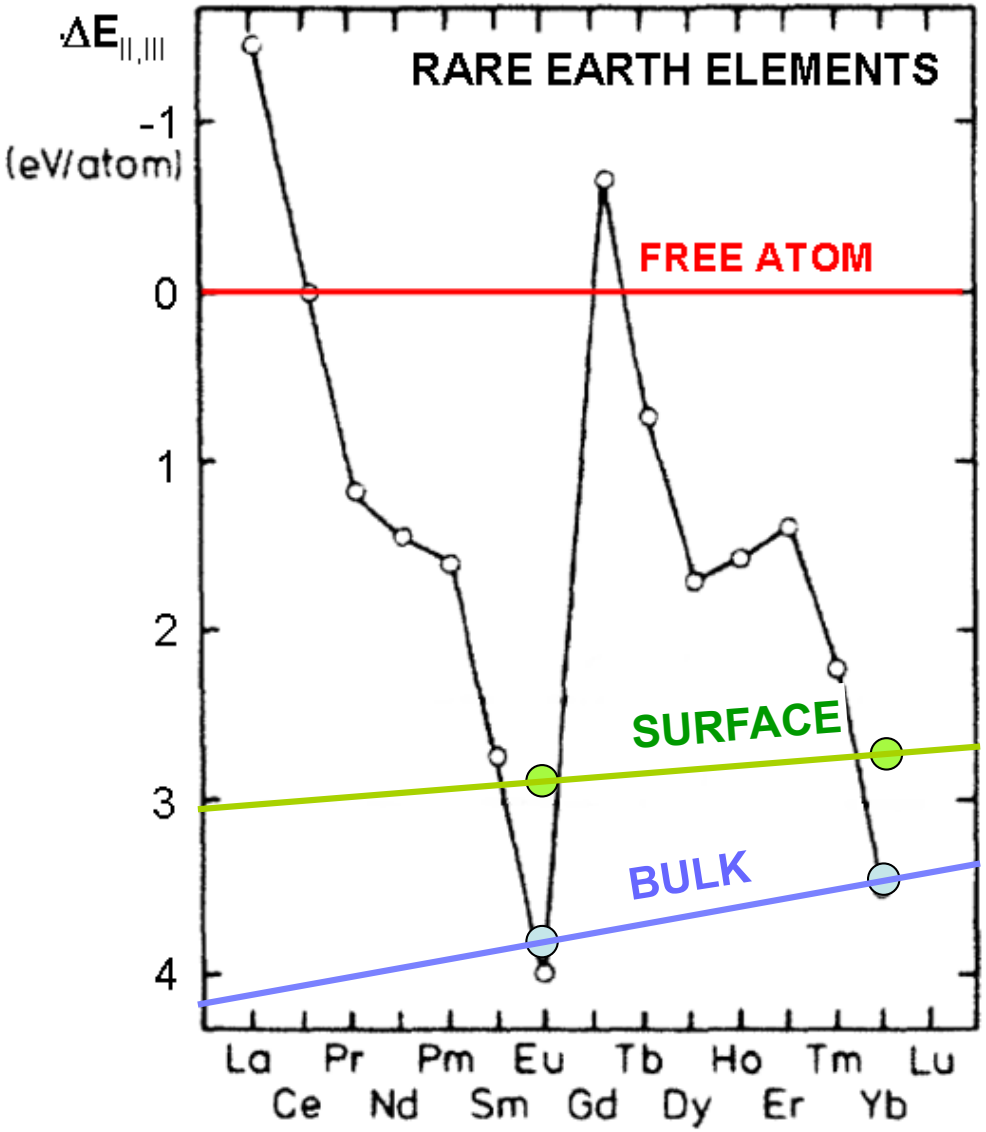
E_{BIN} ≈ 0,2 eV,

E_{BIN}^{surf} ≈ 1,0 eV

Prediction for whole series:

All RE except Eu, Yb trivalent in the bulk and at the surface!

Inclination of lines due to different atomic volumes!



Photoemission of 4f-states

$RERh_2Si_2$ compounds:

RE = Yb: mixed-valent

E_{BIN} ≈ 0 eV,

E_{BIN}^{surf} ≈ 0,7 eV

RE = Eu: divalent

E_{BIN} ≈ 0,2 eV,

E_{BIN}^{surf} ≈ 1,0 eV

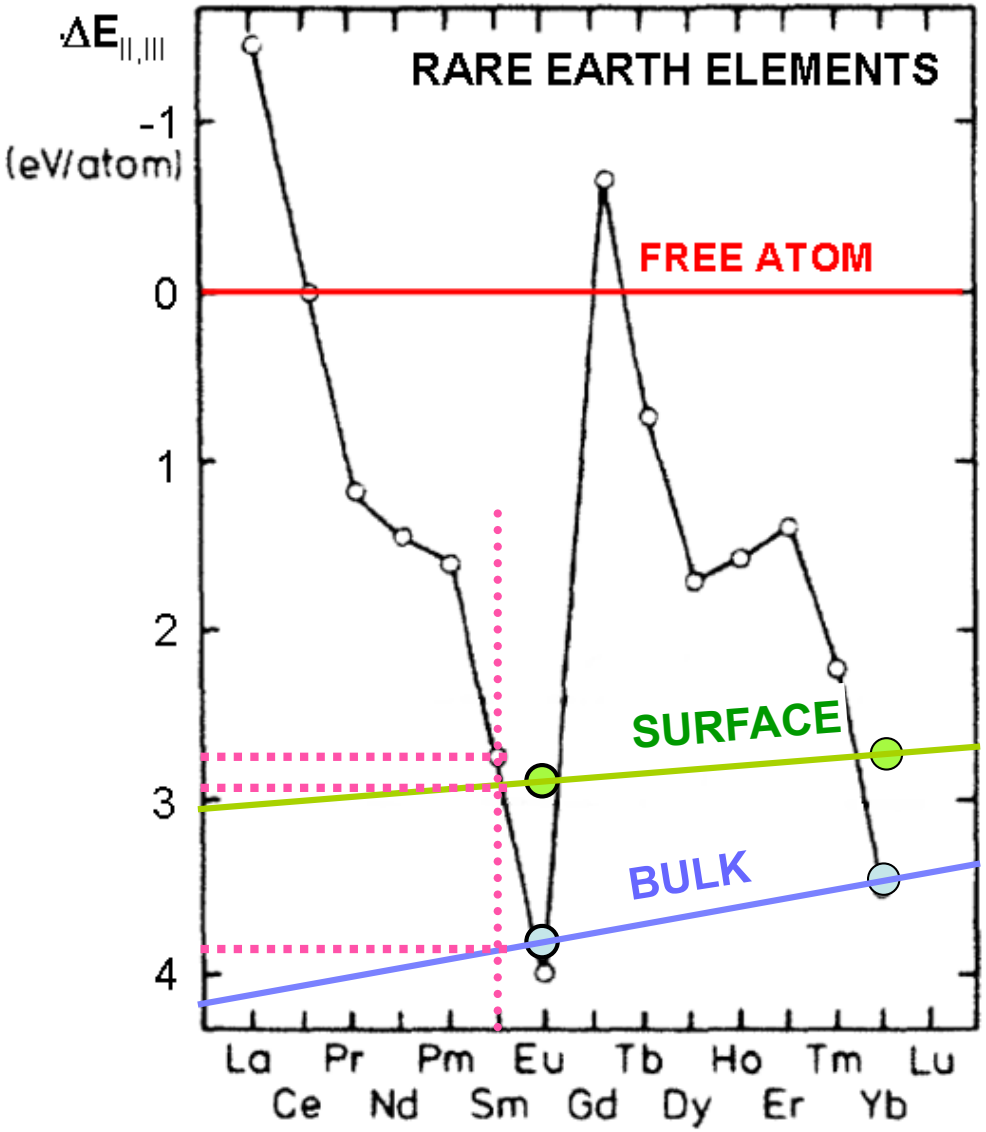
Prediction for whole series:

All RE except Eu, Yb trivalent in the bulk and at the surface!

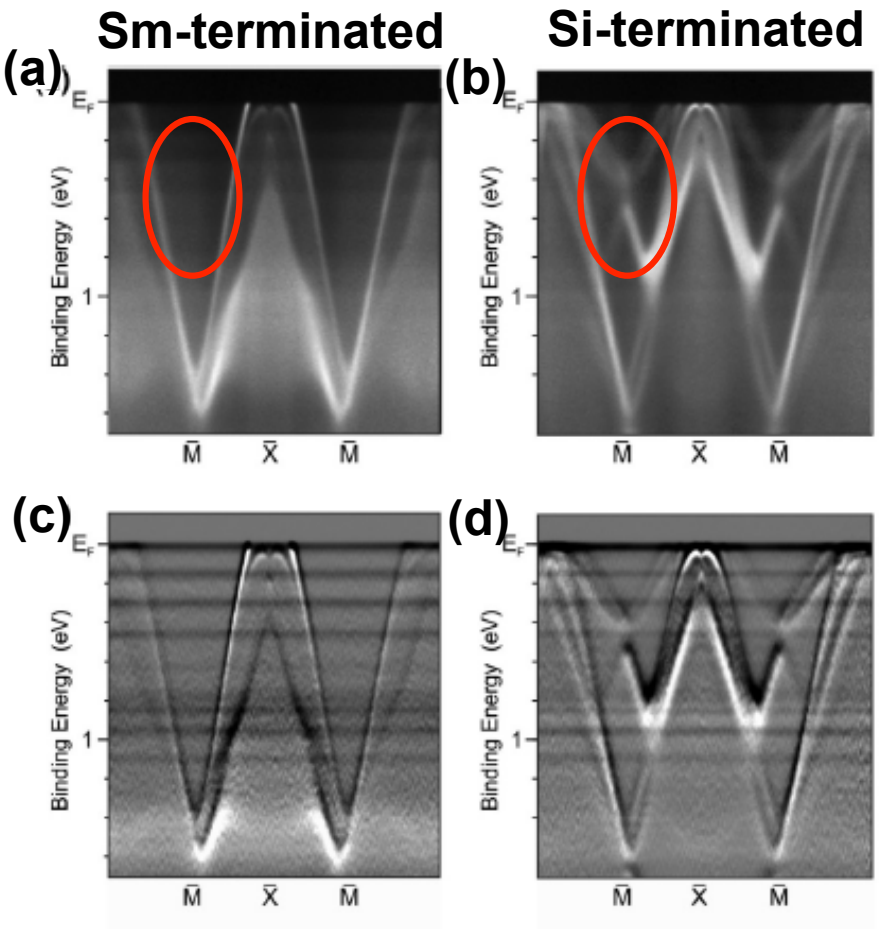
RE = Sm; E_{BIN} ≈ -1,1 eV

E_{BIN}^{surf} ≈ -0,2 eV

Trivalent in the bulk and at the surface



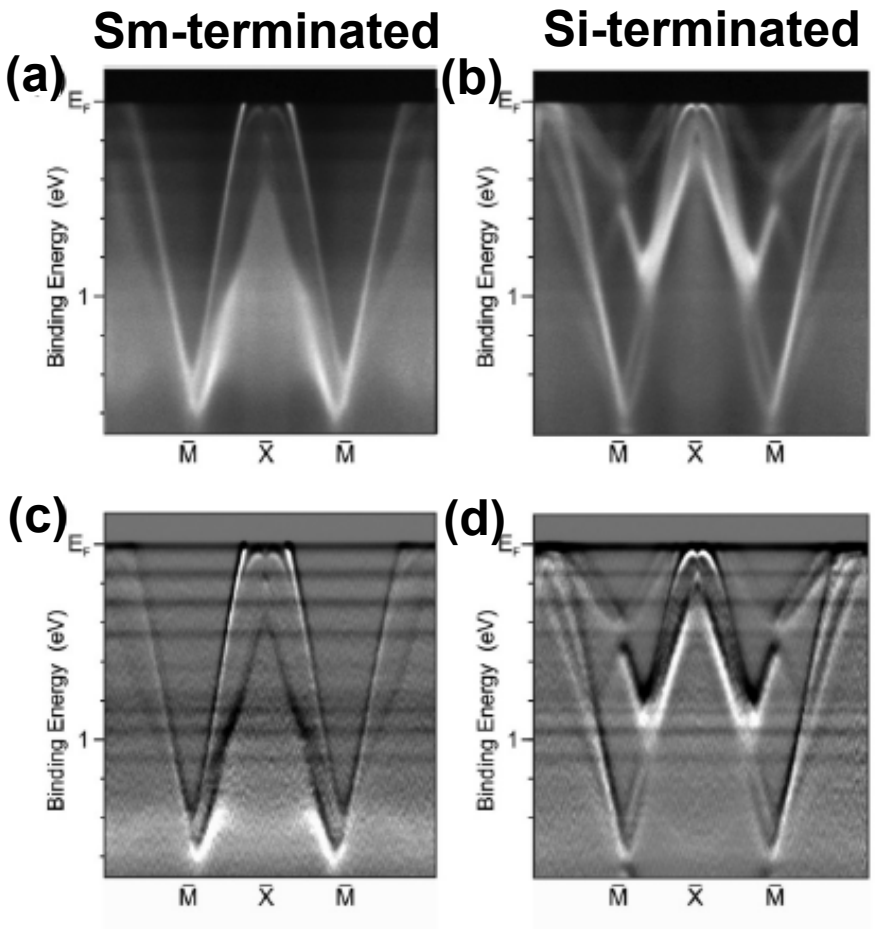
$SmRh_2Si_2$

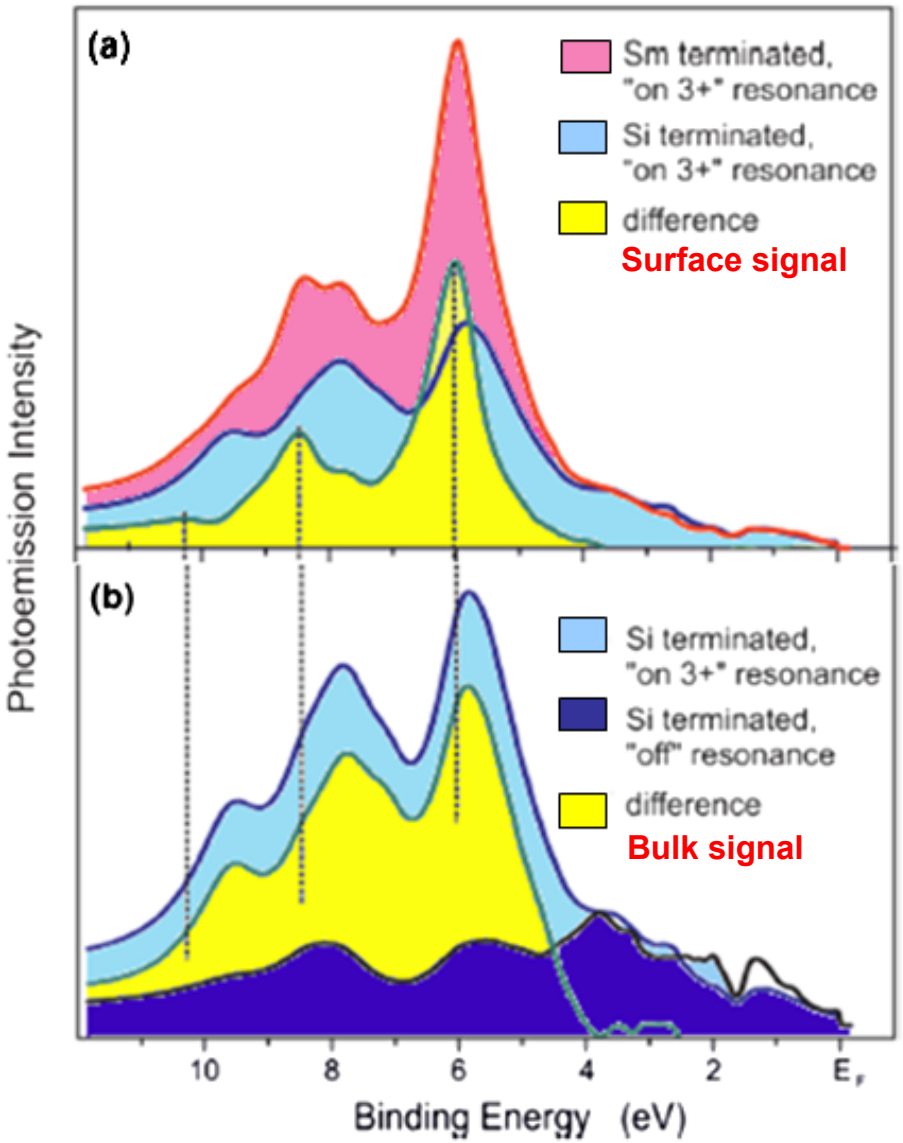


- Si-termination identified by surface state around M-point

A. Chikina et al., PRB 95, 155127 (2017)

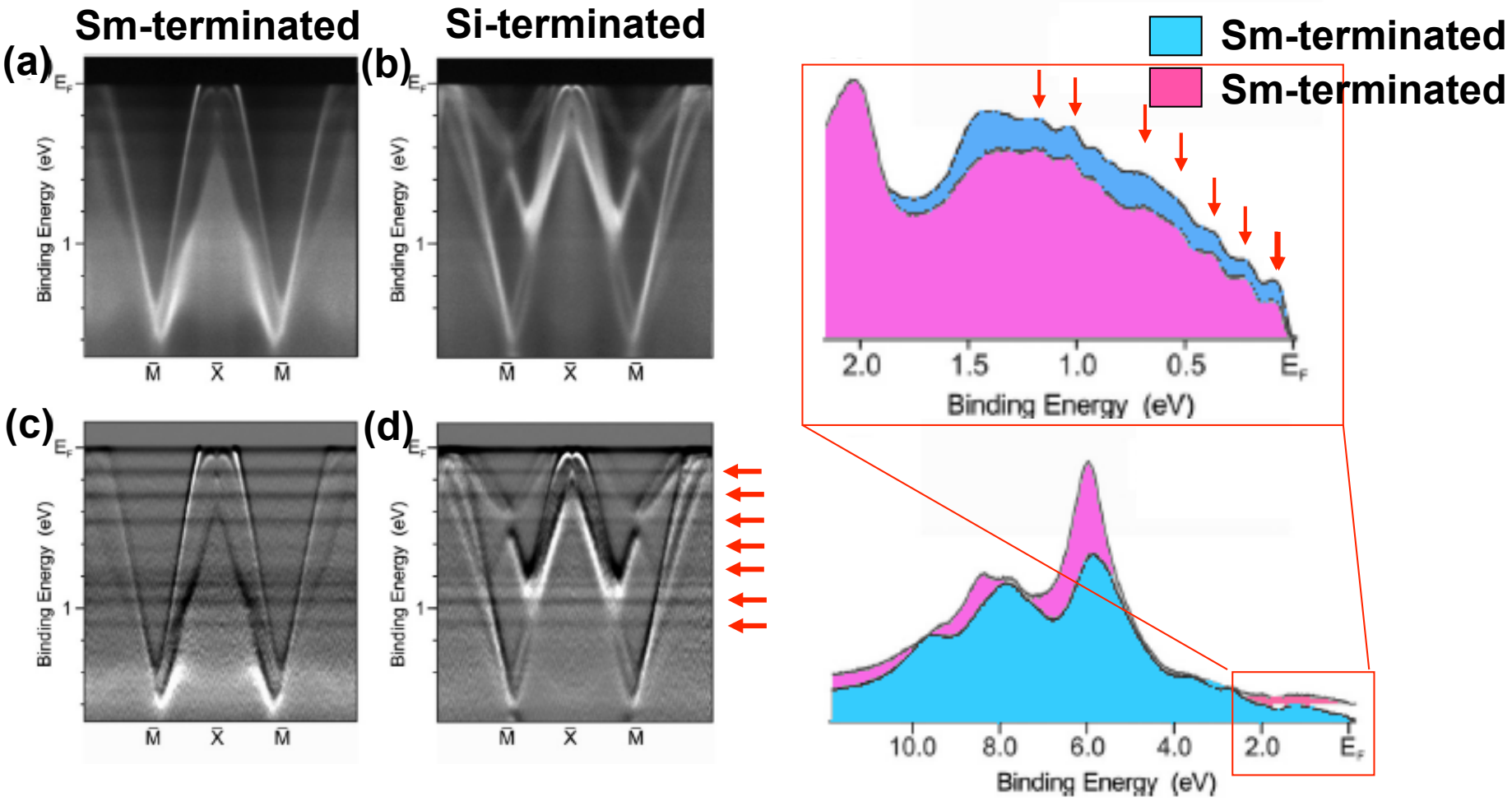
$SmRh_2Si_2$





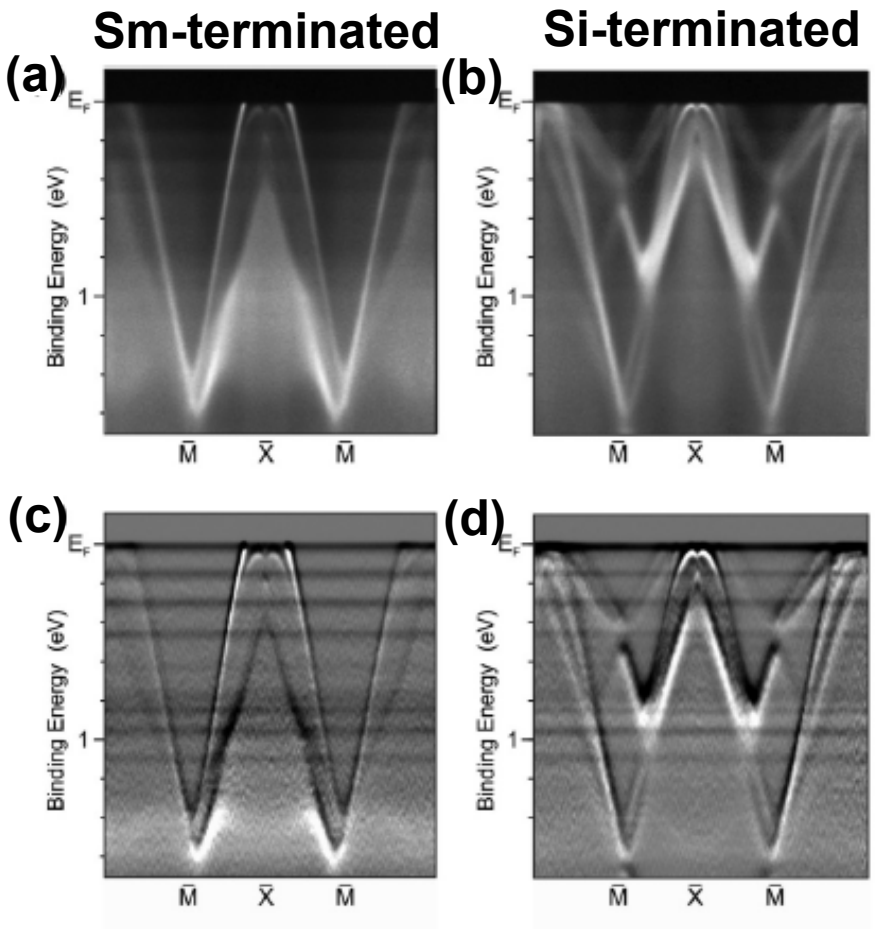
- Si-termination identified by surface state around M-point
- Bulk and surface spectra dominated by $4f^4$ multiplets
- Clear surface-shift of $4f^4$ multiplet → **almost trivalent in the bulk and at the surface**
  Bulk signal broadened by hybridization, surface shift 0.3-1.0 eV

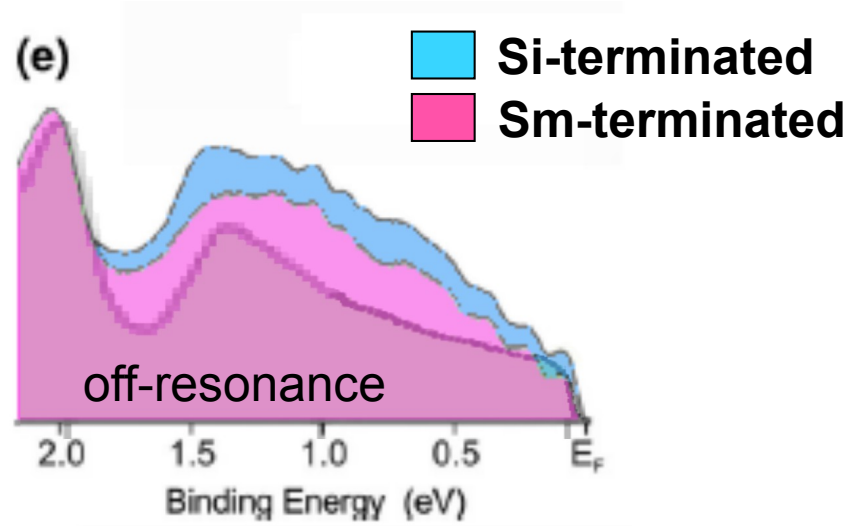
$SmRh_2Si_2$

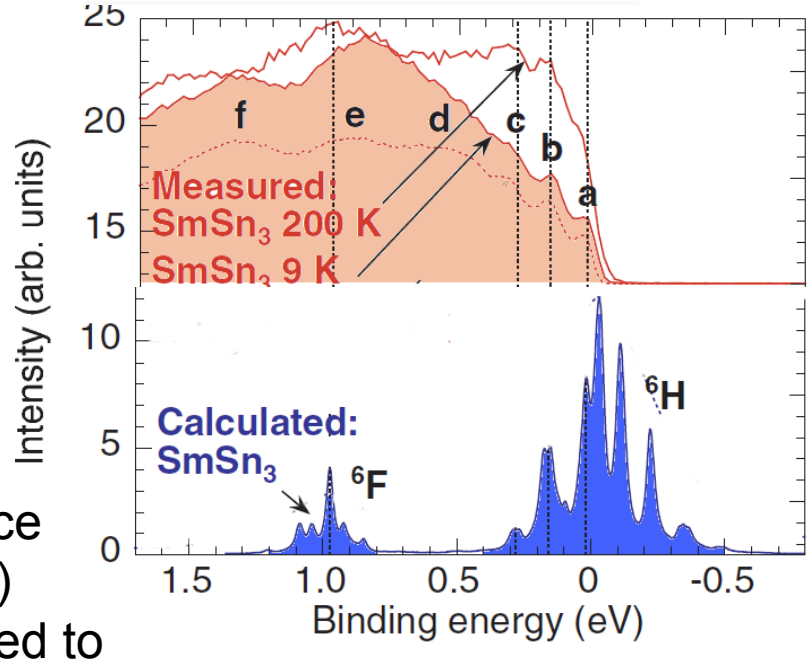


- Si-termination identified by surface state around M-point
- Bulk and surface spectra dominated by $4f^4$ multiplet
- Clear surface-shift of $4f^4$ multiplet → almost trivalent in the bulk and at the surface
- Non-dispersive stripe-structure near E_F → additional $4f^5$ multiplet?

$SmRh_2Si_2$

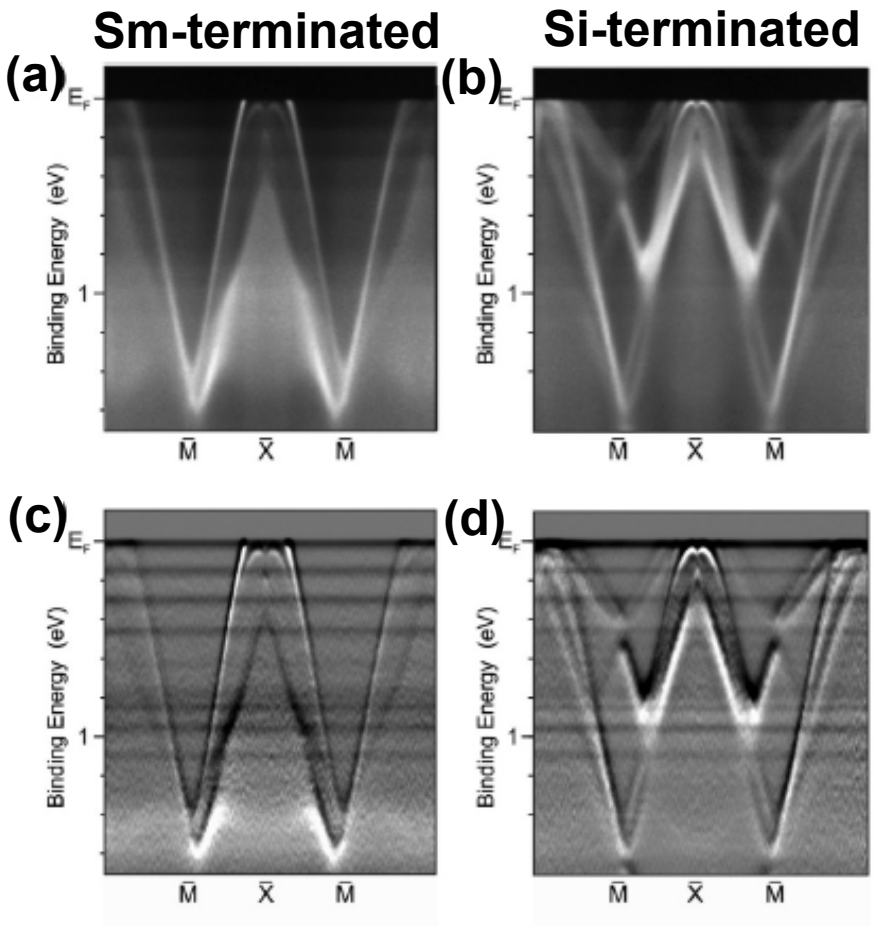


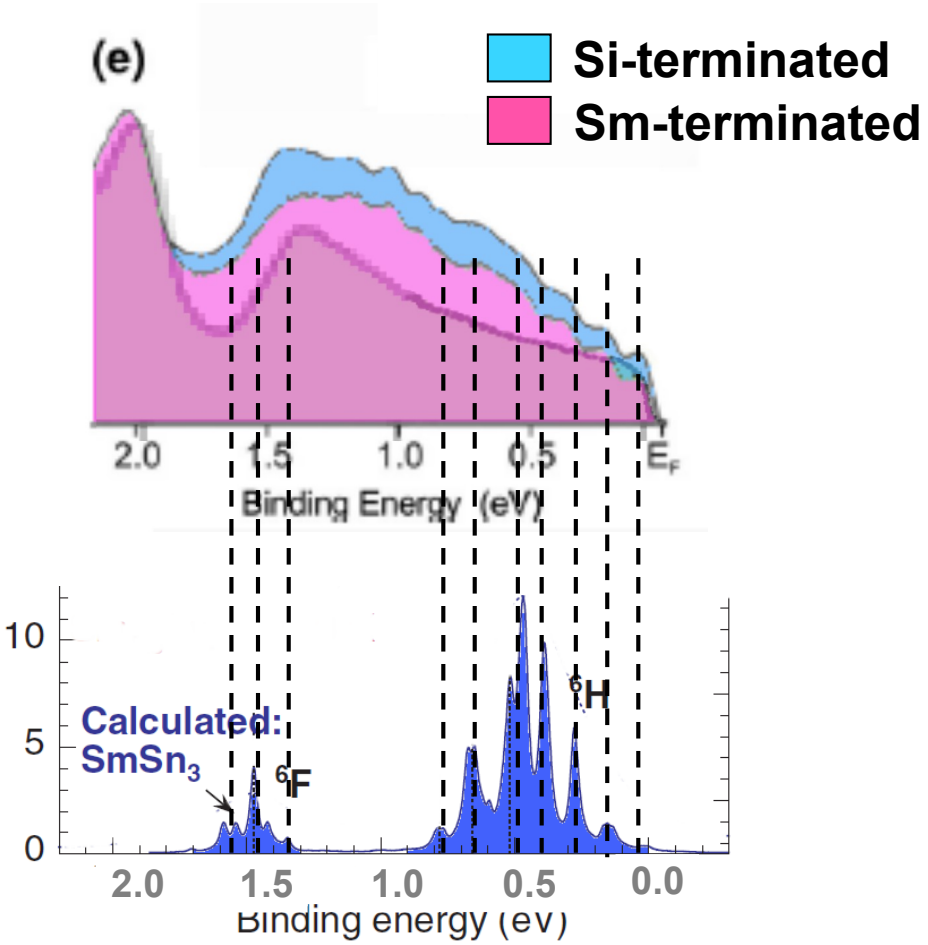


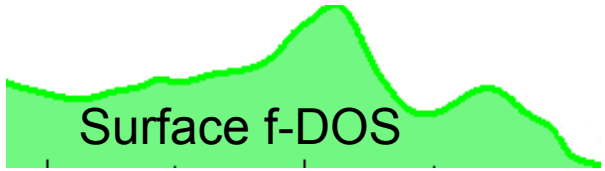


- Spectral shape similar for bulk and surface
- H. Yamaoka et al, PRB **85**, 115120 (2012)
  Similar stripes observed in $SmSn_3$ assigned to **shifted $4f^5$ multiplet**

$SmRh_2Si_2$



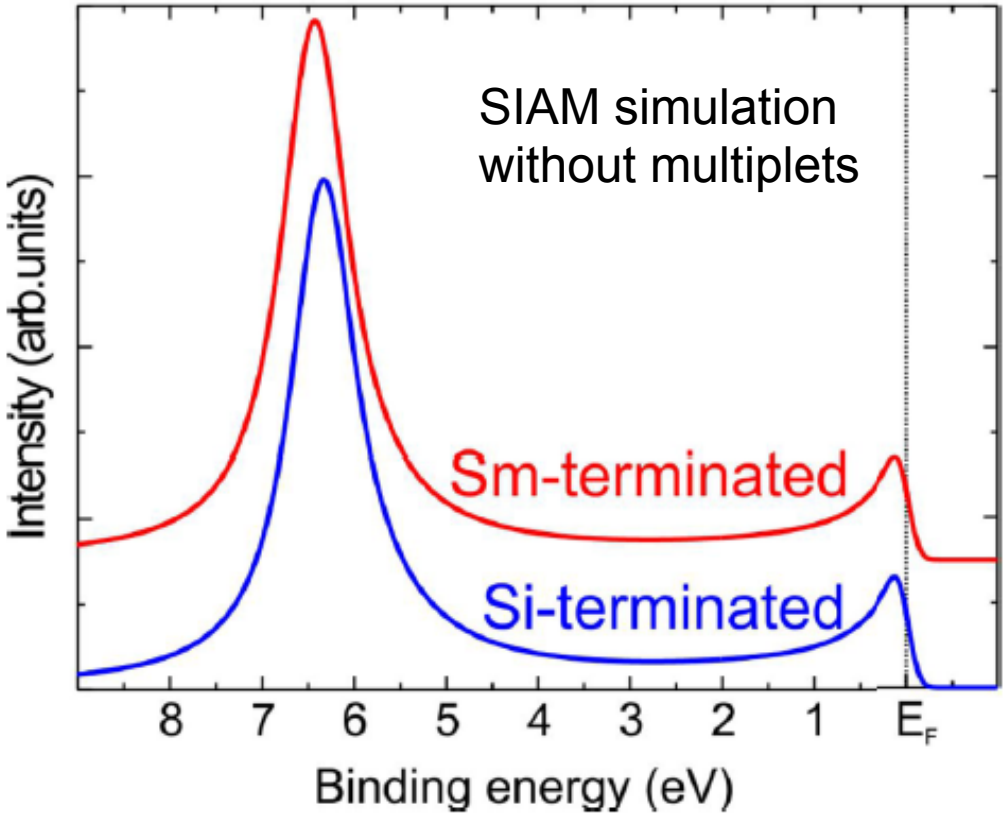




- For mixed-valent Sm $4f^5$-multiplet must be pinned at E_F both for bulk and surface
- Intensity of individual multiplet terms may be altered due to resonance
- **Mixed-valent in the bulk and at the surface** with mean valence around 2.9

Sm-valence in $SmRh_2Si_2$: SIAM

- Neglect of multiplet effects and double-excitations
- Estimation of Δ-parameter from interpolation between Ce- and Yb-system
  Bulk: Δ = 0.7 eV
- Assumption: Reduction of Δ at surface to 70% of bulk value
- Setting $\varepsilon = -E_{BIN}(4f^4)$
  Bulk: ε = -6.0 eV
  Surface: ε = -6.3 eV
- With U_{ff} = 7 eV from LDA+U we get for $-E_{BIN}(4f^5) \approx \varepsilon + U_{ff}$
  Bulk: E_{BIN} = -1.0 eV (-1.1 eV)
  Surf: E_{BIN} = -0.7 eV (-0.3 eV)
  thermochemical estimate in parentesis



Result of SIAM:

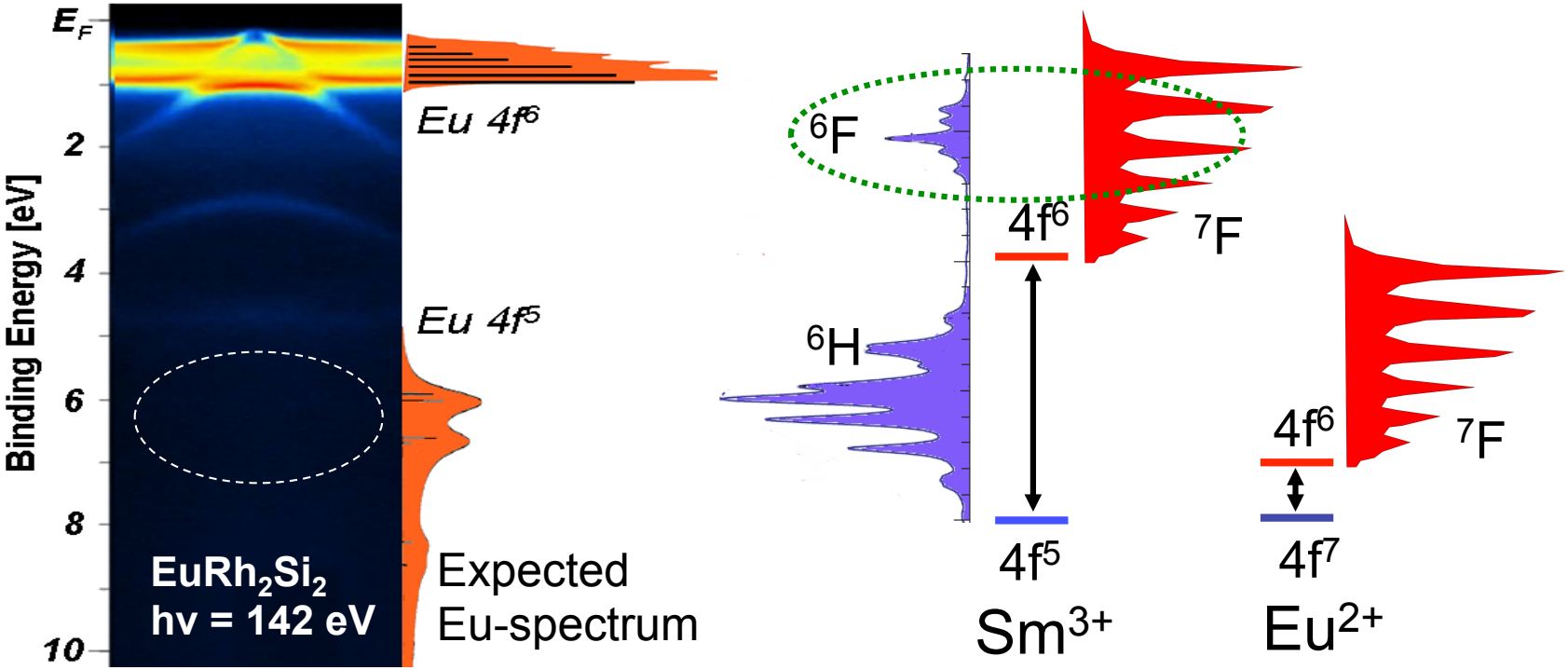
Bulk: mean Sm-valence: 2.94

Surface: mean Sm-valence: 2.95

Behavior qualitatively similar to Ce!

Why is $EuRh_2Si_2$ stable divalent?

- Assuming for **Eu similar Δ as for Sm** and ε = 0.2 eV
  → **$EuRh_2Si_2$** should be mixed-valent, **mean valence ~2.5**!
- Photoemission: **No trace of $4f^5$ final-state** multiplet characteristic for Eu^{3+}



- Hopping directly or via virtual low-energy excitations of $4f^n$-configurations
- Sm: Strong overlapp of $4f^5$ ^6F and $4f^6$ ^7F terms
- Eu: No low-energy excitations possible in $4f^7$ (spin-flip requires $\Delta E > 4$ eV)
  → hybridization strongly reduced! **A. Chikina et al., PRB 95, 155127 (2017)**

Summary:

- clear determination of surface termination by inspection of surface state characteristic for Si-termination
- different degree of 4f-hybridization in the bulk and at the surface:

  $YbRh_2Si_2$: bulk intermediate valent close Yb^{3+}, surface stable divalent

  $CeRh_2Si_2$: strongly hybridized in the bulk, weakly at the surface
- estimation of surface valence by means of thermochemical model

  $SmRh_2Si_2$: bulk and surface intermediate valent close to Sm^{3+}

  - explanation whithin SIAM in analogy to Ce-compounds
  - possible Kondo-phenomena in Sm-compounds ?

  $EuRh_2Si_2$: bulk and surface stable divalent, although mixed-valence expected from analogy to Sm-compound

  - strongly reduced hybridization due to lacking low-energy multiplet ?
  - phenomenon generally encountered in Eu-compounds, where in contrast to weak T-dependent valence changes in Yb and Ce-systems strong abrupt 1^{st}-order transitions take place upon T or p-changes