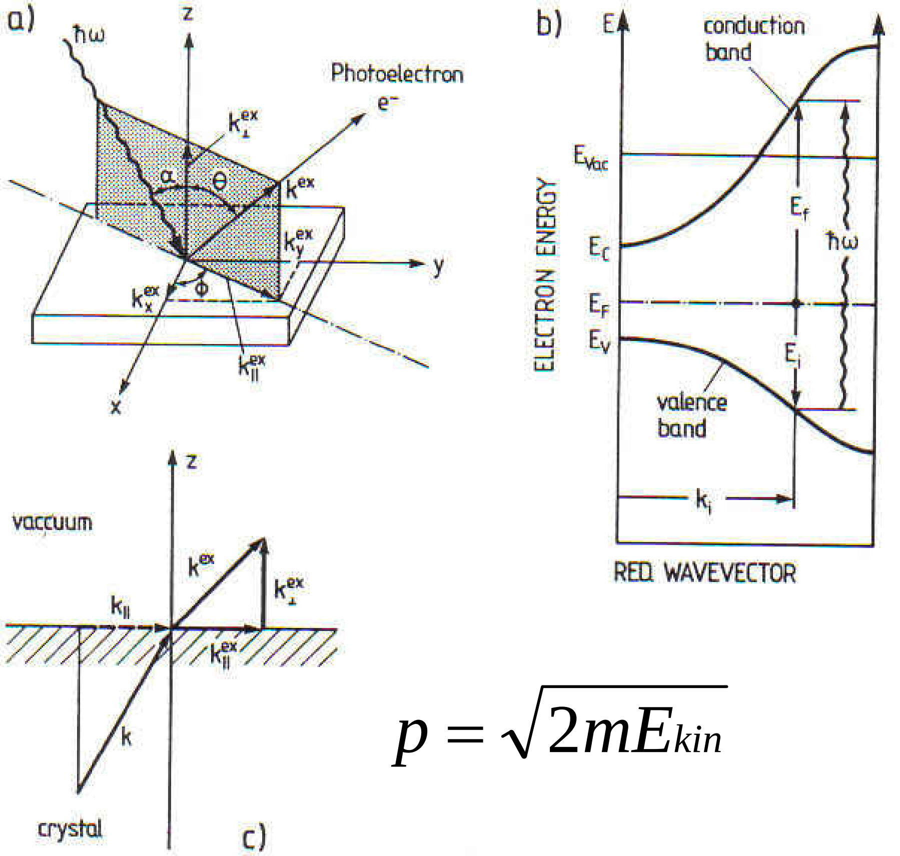
PhotoEmission Spectroscopy



$$p = \sqrt{2mE_{kin}}$$

Fig. 6.6a–c. Description of a photoemission experiment. (**a**) Definition of the angles and wave vectors of the incident photon ($\hbar\omega$) and emitted electron (e^-). (**b**) Representation of the photoexcitation process in the electronic band scheme $E(\mathbf{k})$ of a semiconductor. Only direct transitions with $\mathbf{k}_i \simeq \mathbf{k}_f$ are taken into account. The energies of the initial state (E_i) and final state (E_f) are referred to the Fermi level E_F. (**c**) Conservation of the wave vector component $\mathbf{k}_\parallel$ (parallel to the surface) upon transmission of the emitted electron through the surface

PES: Band-Structure ans Surface State

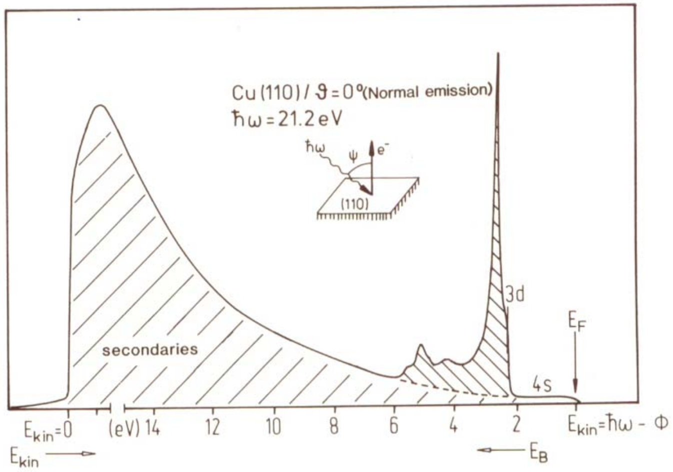


Fig. 1.7. UPS (He I, $\hbar\omega = 21.2\,\mathrm{eV}$) spectrum from a (110) face of Cu (normal emission, $\vartheta = 0$, ϑ being the polar angle with respect to the surface normal). The flat 4s band and the structured 3d band are seen. The cutoff marks the point where $E_{\mathrm{kin}} = 0$ and via (1.2) the work function can then be derived

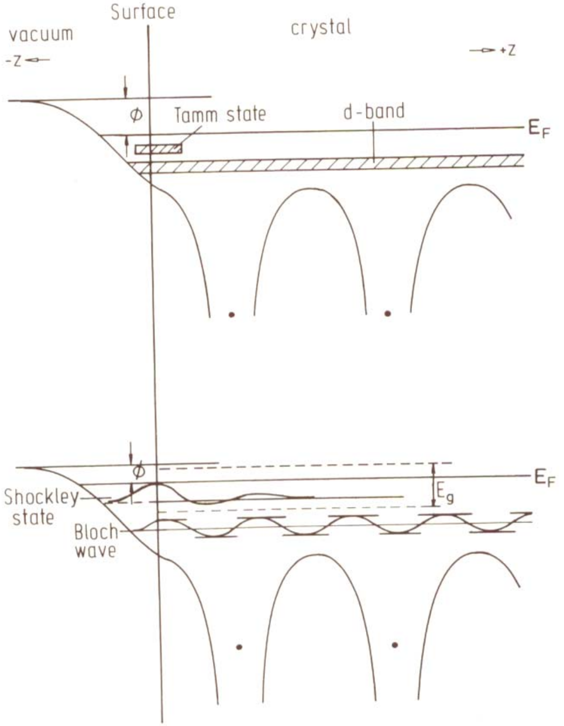


Fig. 8.4. Tamm and Shockley states. The Tamm state (*top*) is split-off from a band (e.g., a d band) of the crystal by the change in potential at the surface. A Shockley state (*bottom*) is a state created in a gap of the bulk-band structure due to the termination of the crystal by a surface (semi-infinite crystal)

PES: Surface State

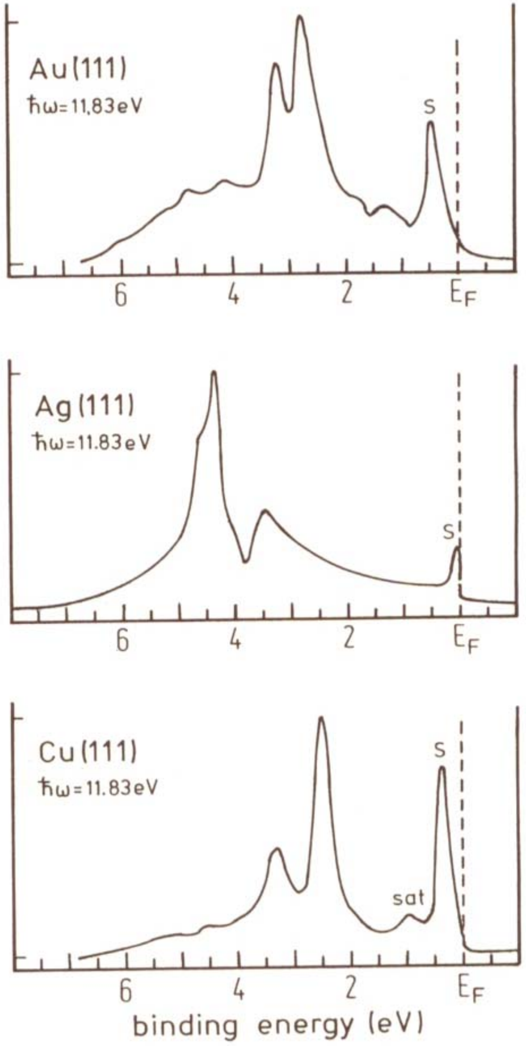


Fig. 8.7. UPS spectra of the (111) surfaces of Cu, Ag and Au with $\hbar\omega = 11.83\,\mathrm{eV}$. For all three metals a surface state (label S) is observed near E_F in the so-called L-gap at $E_F \le E_S \le 1\,\mathrm{eV}$, see Fig. 8.6 [8.24]

Angle Resolved PhotoEmission Spectroscopy

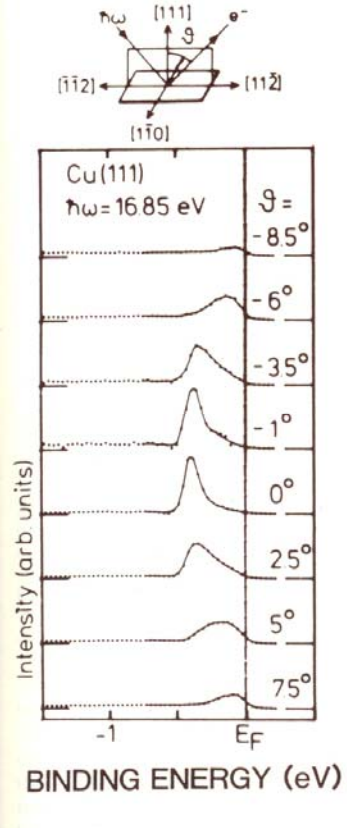
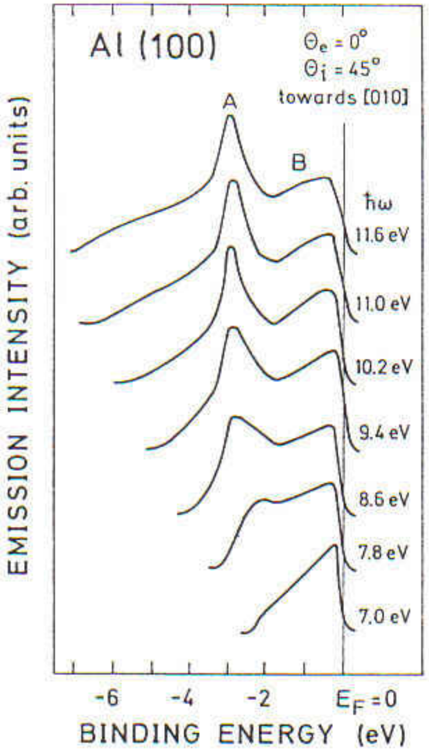


Fig. 8.8. Measurement of the dispersion of the L-gap surface state for Cu(111) (near normal emission, $\hbar\omega = 16.85\,\mathrm{eV}$) The emission direction is in a $(1\bar{1}0)$ plane and it is tilted towards $[\bar{1}\bar{1}2]$ and $[11\bar{2}]$. In going away from the normal the surface state disperses towards the Fermi energy. The $\vartheta = 0$ energy is the same as in Fig. 8.7, ($\hbar\omega = 11.83\,\mathrm{eV}$), indicating that one is indeed observing a surface state. Note that the contribution of the satellite of the Ne I radiation to the spectra has been subtracted from the measured experimental data [8.25]



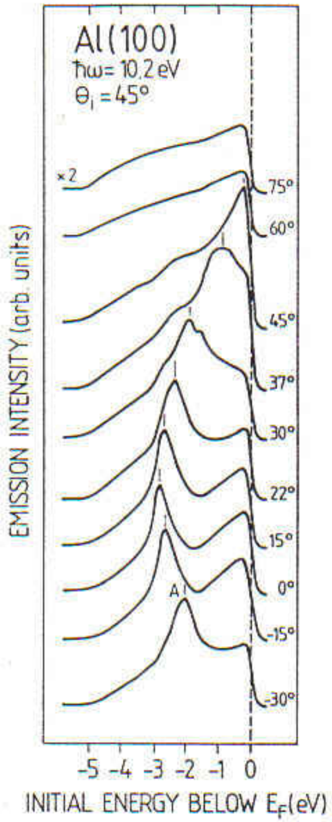


Fig.6.12. Experimental spectra of photoelectrons emitted normal to the Al(100) surface for photon energies between 7 and 11.6 eV (direction of incidence 45° to the [011] direction) [6.12]

Fig.6.13. Photoemission spectra from the Al(100) surface with different polar angles in the $(01\bar{1})$ plane; photon energy $\hbar\omega = 10.2\,\mathrm{eV}$, direction of incidence 45° to the [011] direction [6.12]

Winkelaufgelöste Messungen, erlauben die Bestimmung der Oberflächen-Bandstruktur. Ferner können Oberflächenzustände von Bulk-Zuständen Unterschieden werden. Oberflächenzustände hängen nicht von $k_\perp$ ab und fallen oft in ein Gap der Bulkzustände.

ARPES: Surface States

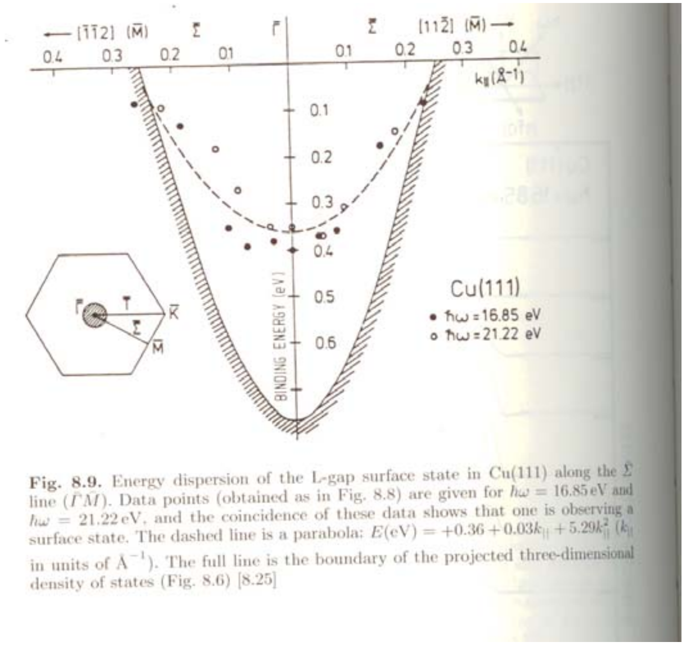


Fig. 8.9. Energy dispersion of the L-gap surface state in Cu(111) along the $\bar{\Sigma}$ line ($\bar{\Gamma}\bar{M}$). Data points (obtained as in Fig. 8.8) are given for $\hbar\omega = 16.85\,\mathrm{eV}$ and $\hbar\omega = 21.22\,\mathrm{eV}$, and the coincidence of these data shows that one is observing a surface state. The dashed line is a parabola: $E(\mathrm{eV}) = +0.36 + 0.03k_{\|} + 5.29k_{\|}^2$ ($k_{\|}$ in units of $\mathrm{\AA}^{-1}$). The full line is the boundary of the projected three-dimensional density of states (Fig. 8.6) [8.25]

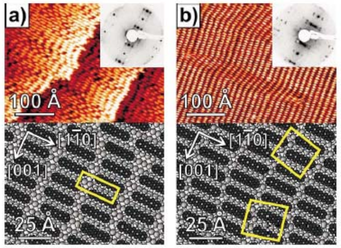


FIG. 1. (Color online) Observed adlayer structures for submonolayer and monolayer coverages of pentacene on Cu(110): (a) 0.8 ML; (b) 1.0 ML. Top: STM images 30 × 40 nm^2. Insets: corresponding LEED patterns taken at (a) 53.5 and (b) 63.0 eV. Bottom: structural models with unit cells marked in pale gray (yellow).

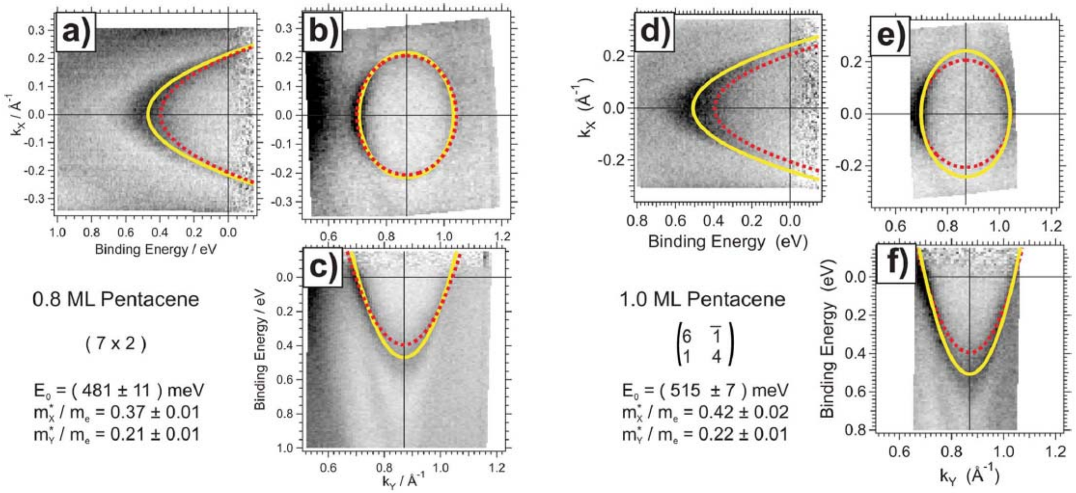


FIG. 3. (Color online) Dispersion of the $\bar{Y}$ surface state of a Cu(110) surface, covered with (a)–(c) 0.8 ML pentacene and (d)–(f) 1.0 ML pentacene. The straight lines marked in pale gray (yellow) mark the fit of a paraboloid to the experimental data. The dotted lines marked in gray (red) correspond to the paraboloid fitted to the experimental data of the clean Cu(110) surface from Fig. 2.

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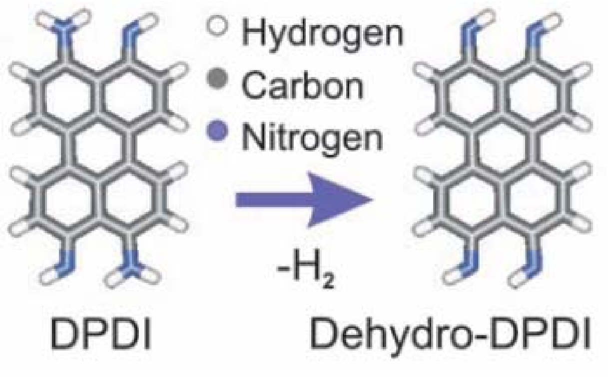
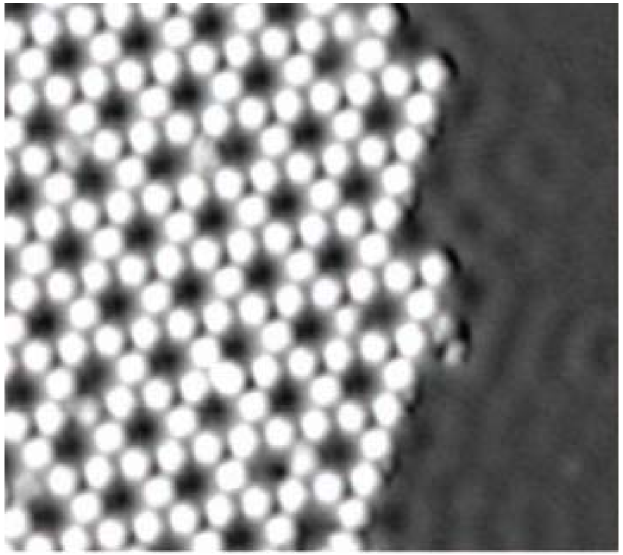
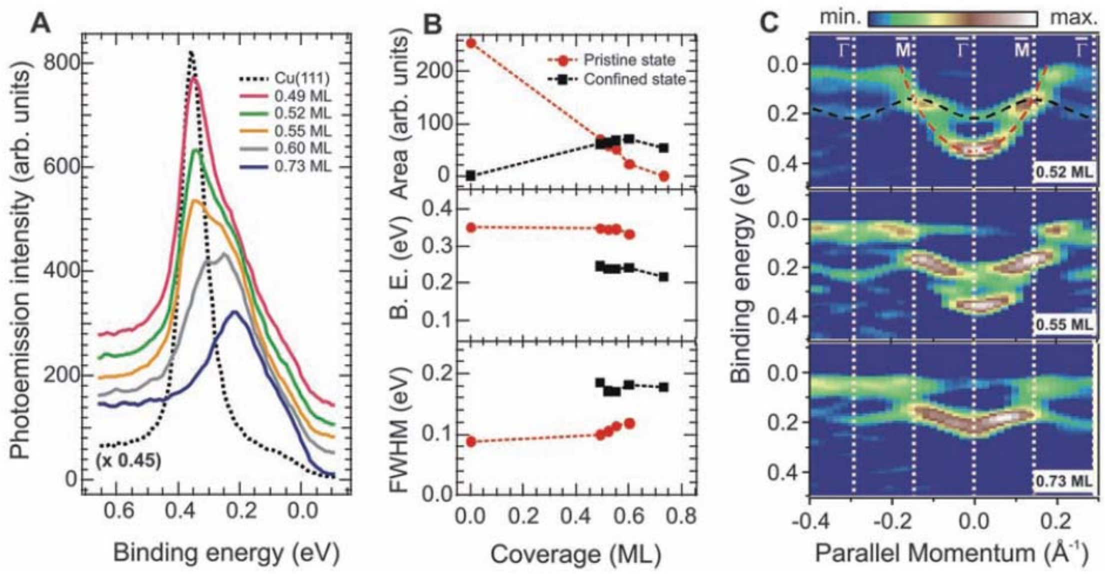
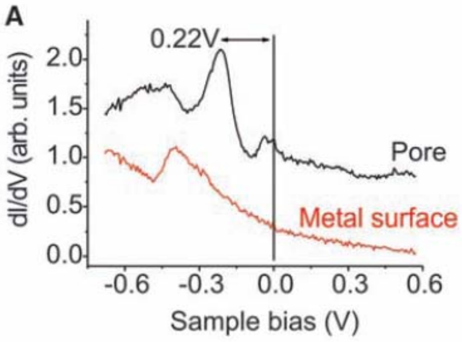
ARPES: Coupled Quantum Dots from Nanoporous Network on Cu(111)









Science 2009, 325, 300

IPES: Inverse PhotoElectron Spectroscopy

Bestimmung der Zustandsdichte der unbesetzten Zustände. Einstrahlung von Elektronen und Messung von Photonen. Zwei Moden: 1. Bremstrahlenspektroskopie: Konstante Elektronenenergie, energieaufgelöste Messung des Lichtes. 2. Isochromate spectroscopy: Elektronenenergie wird variiert. Nur Licht aus einem bestimmten Wellenlängenbereich wird gemessen. Spezieller Bandpassfilter (CaF_2 oder SrF_2-Fenster kombiniert mit Geiger-Zähler mit He gefüllt, sowie einigen J-Kristallen). Vorteil: Grosser Akzeptanzwinkel.

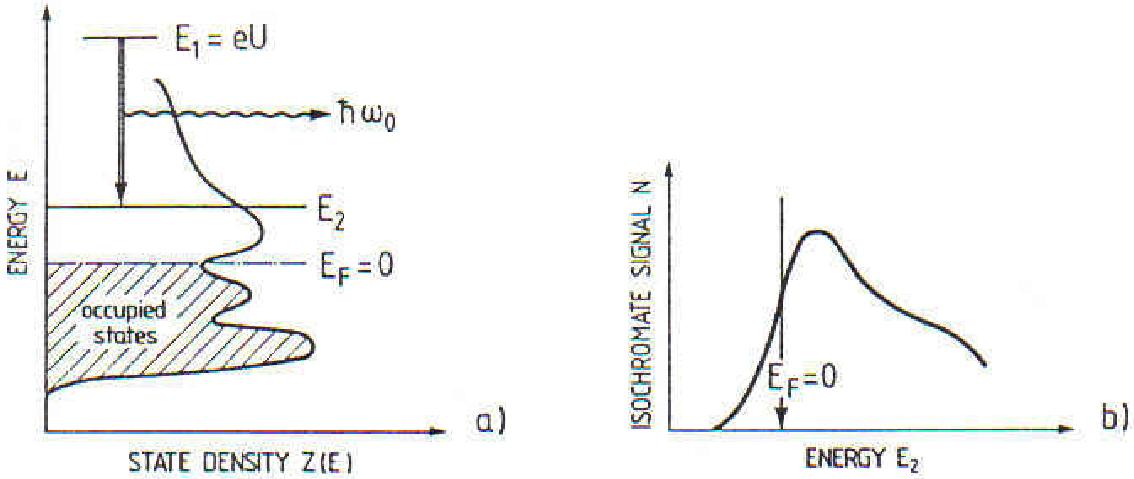


Fig. XI.6. **(a)** Schematic representation of the inverse photoemission process. An electron injected from outside the crystal enters an excited electronic state E_1 (=eU if an external voltage U accelerates the electrons onto the sample); the electron is deexcited into a state E_2 and the corresponding energy is emitted as a photon of energy $\hbar\omega_0 = E_1 - E_2$. **(b)** Schematic isochromate spectrum $N(E_2) \propto Z(E_2)$ as obtained according to **(a)**

IPES of Cu(100)

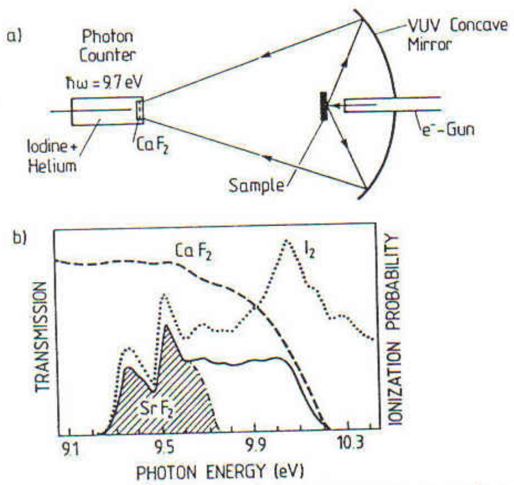


Fig. XI.7. **(a)** Inverse photoemission set-up using a Geiger counter (isochromate spectroscopy). The UV radiation emitted from the sample is focussed onto the window of a Geiger photon counter. **(b)** The spectral window of the detector is determined by the spectral transmittance of the counter window (SrF_2 or CaF_2) and by the spectral dependence of the ionization process of iodine [XI.5, 6]

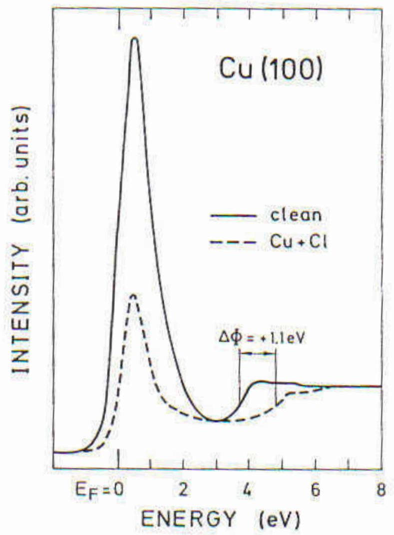


Fig. 6.28. Inverse photoemission (isochromate) spectrum on a Cu(100) surface, clean (*full line*) and after adsorption of chlorine (*broken line*). The energy scale extends from the Fermi level E_F up towards the vacuum level [6.27]

Summary: PES and IPES

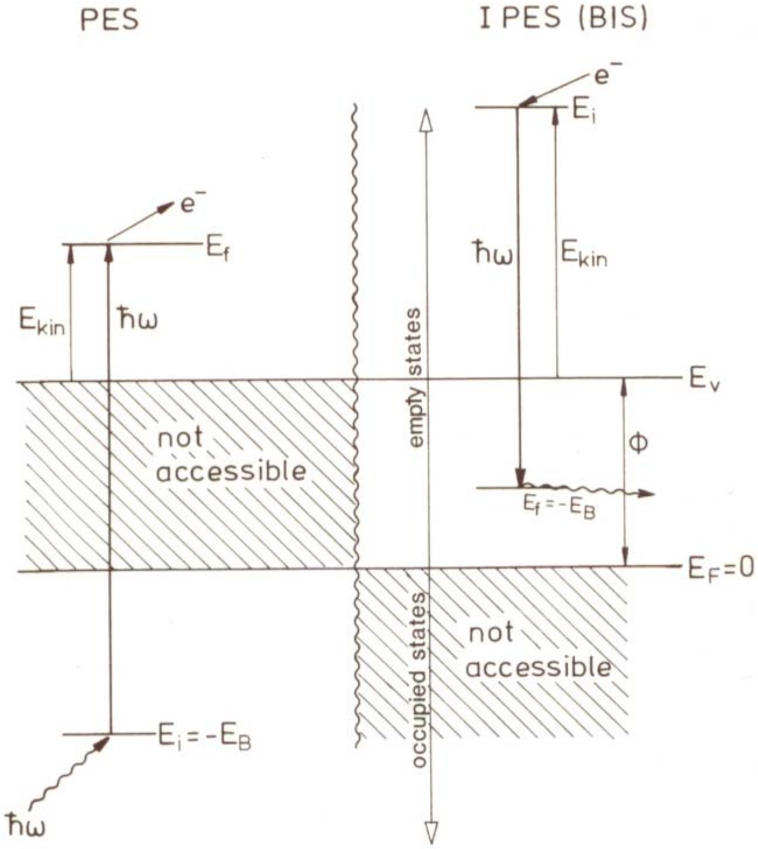


Fig. 9.1. Schematic diagram of PhotoEmission Spectroscopy (PES) and Inverse PhotoEmission Spectroscopy (IPES). In PES the energy range between the Fermi energy and the vacuum level is not accessible, while in IPES the unaccessible range is that below E_F. Thus the two techniques complement each other

Further Reading

1. **Surface Analysis** by Vickermann and Gilmore (Eds)
2. **Photoelectron Spectroscopy** by Huefner
3. **Surface Analysis by Auger and XPS** by Briggs and Grant (Eds.)

Surface Physics 2010

Surface Diffusion

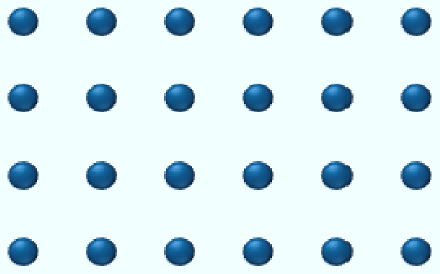
UNI
BASEL

Lecturer: Dr. Enrico Gnecco

NCCR Nanoscale Science

Random-Walk Motion

- Thermal motion of an adatom on an ideal crystal surface:



- Thermal excitation → the adatom can hop from one adsorption site to the next

- Mean square displacement at time *t*:

$$\boxed{\langle \Delta r^2 \rangle = \nu a^2 t}$$

a = jump distance; ν = hopping frequency

(Note that νt = number of hops!)

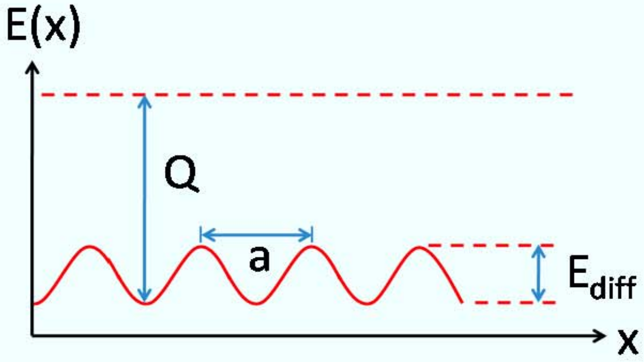
- **Diffusion coefficient**:

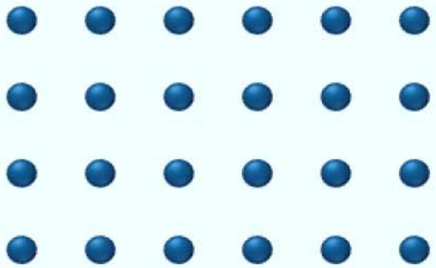
$$\boxed{D = \frac{\langle \Delta r^2 \rangle}{zt} = \frac{\nu a^2}{z}}$$

$$z = \text{number of first neighbors} = \left[\begin{array}{l}\text{2 in 1D diffusion}\\ \text{4 on a square lattice}\\ \text{6 on a hexagonal lattice}\end{array}\right.$$

Random-Walk Motion

- Hopping → surmounting a potential barrier





- **Arrhenius law**:

$$\boxed{\nu = \nu_0 \exp\left(-\frac{E_{diff}}{k_B T}\right)}$$

ν_0 = oscillation frequency of the atom in the well;

E_{diff} = barrier height

Tipically E_{diff} ~ 5-20% of Q (heat of desorption)

- For chemisorbed species: $E_{diff} >> k_B T$
- If $E_{diff} < k_B T$: 2D gas (only a few physisorbed species)

Fick’s Laws

- **Fick’s First Law** (for 1D diffusion):

$$\boxed{J = -D\frac{\partial c}{\partial x}}$$

diffusion flux

concentration gradient

(flux → region of lower concentration)

- **Fick’s Second Law** (for 1D diffusion):

$$\boxed{\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}}$$

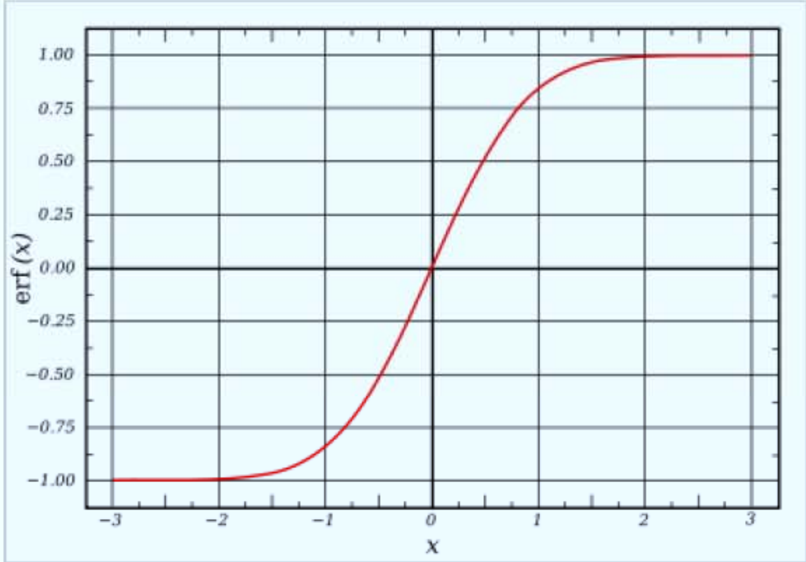
← from equation of continuity

- Analytical solutions can be found for specific initial and boundary conditions!

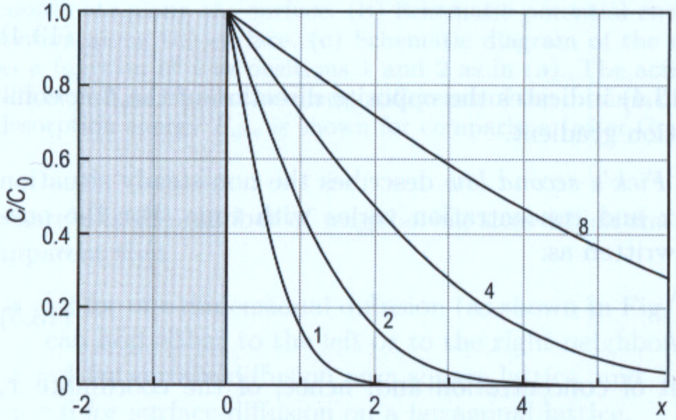
Analytical Solutions of Fick's Laws

- We introduce the **error function**

$$\mathrm{erf}\,(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp(-t^2)\,dt$$



- Source of constant concentration:



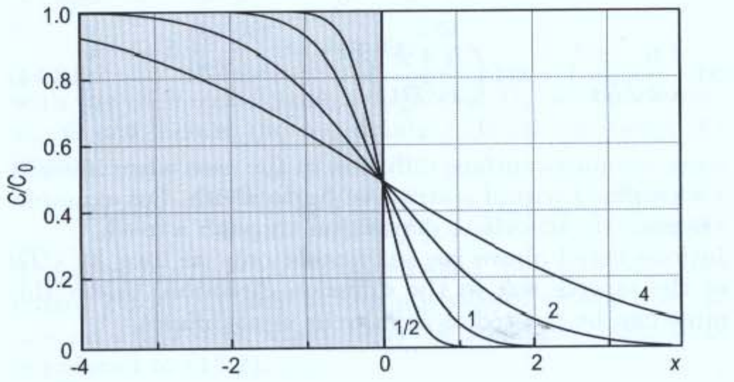
$$c(x,t) = c_0\left[1-\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

$2\sqrt{Dt}$: **diffusion length**

- Example: Submonolayer film with 3D islands supplying mobile adatoms

Analytical Solutions of Fick's Laws

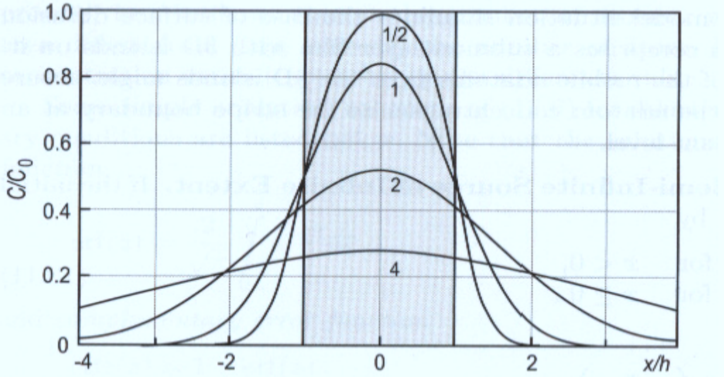
- Source of infinite extent:



$$c(x,t)=\frac{c_0}{2}\left[1-\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right]$$

  - Example: Submonolayer film

- Source of limited extent:



$$c(x,t)=\frac{c_0}{2}\left[\mathrm{erf}\left(\frac{h-x}{2\sqrt{Dt}}\right)+\mathrm{erf}\left(\frac{h+x}{2\sqrt{Dt}}\right)\right]$$

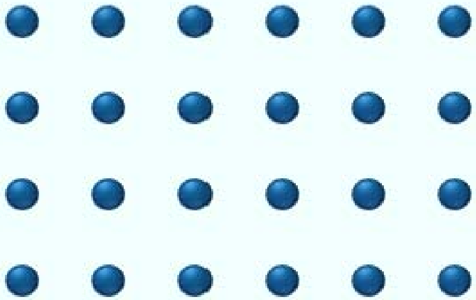
  - Example: Submonolayer film confined in a stripe of finite width

Diffusion Mechanisms

- Depending on the coverage Θ:
  - Tracer diffusion (low Θ)
  - Chemical diffusion (intermediate to high Θ)

Tracer Diffusion

- **Tracer Diffusion:** - Low coverage (<0.01 ML)
  - Individual adparticles



- Fick's first law is valid:

$$D = \frac{\langle \Delta r^2 \rangle}{zt}$$

- For an ensemble of many particles:

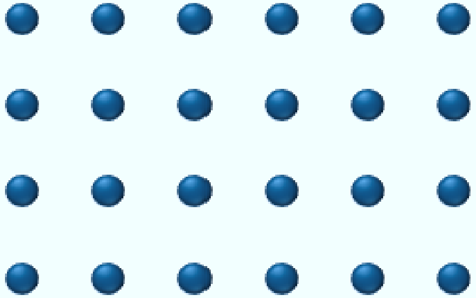
$$D = \frac{1}{zNt} \sum_i \langle \Delta r_i^2 \rangle$$

(no relation to radioactive tracers!)

Chemical Diffusion

- **Chemical Diffusion:** - Higher coverage

  - Attraction or repulsion between adatoms



- Fick's first law can be generalized:

$$J = -\underbrace{D_c(\Theta)}_{\text{chem. diff. coefficient}} \frac{\partial \overset{\text{coverage}}{\Theta}}{\partial x}$$

- <u>Strong dependence on</u> adsorbate <u>coverage</u> is expected, especially when ordered phases are formed (Naumovets-Vedula, 1986)

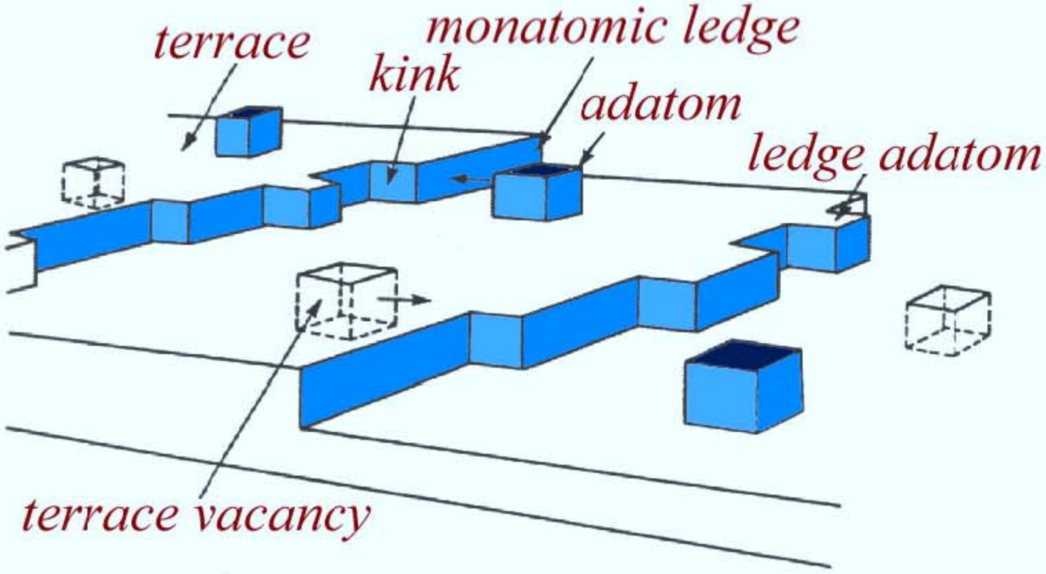
Diffusion Mechanisms

- Depending on the landscape**:**
  - Intrinsic diffusion (no sources and traps)
  - Mass transfer diffusion (generation and/or trapping)

Intrinsic Diffusion

- Adparticle motion is monitored within a single terrace → Spatial limit ~ 100 nm

- In practice: no strong distinction from tracer diffusion



Mass Transfer Diffusion

- Real surfaces contain defects (steps, kinks, adatoms or vacancy clusters, etc.)

- If average separation between defects < diffusion length → number of mobile particles (and diffusion) become strongly temperature dependent

- If adatoms and substrate are the same chemical species:

$$D = \frac{\nu_0 a^2}{z} \exp\left(- \frac{\boxed{\Delta G} + E_{diff}}{k_B T} \right)$$

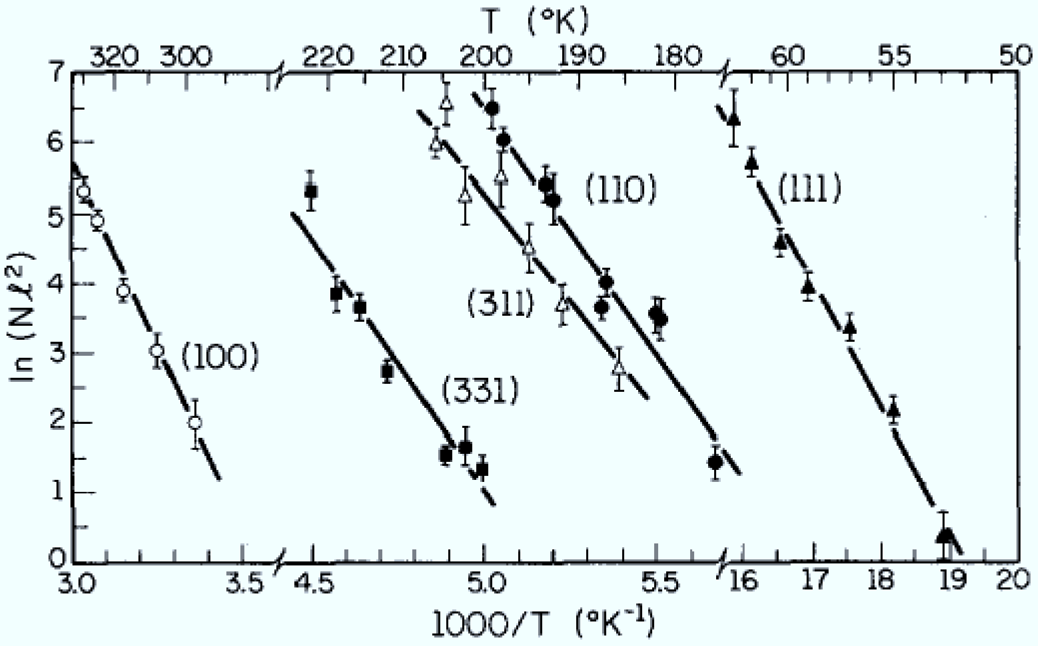
ΔG = energy of adatom formation

(→ two types of energy barriers!)

Anisotropy of Surface Diffusion

- **Orientational Anisotropy:** the diffusion coefficient depends on the orientation of the surface

- Example: Rh surfaces at different T (Ayrault & Ehrlich, JCP 1974)



N: number of jumps in 3 min

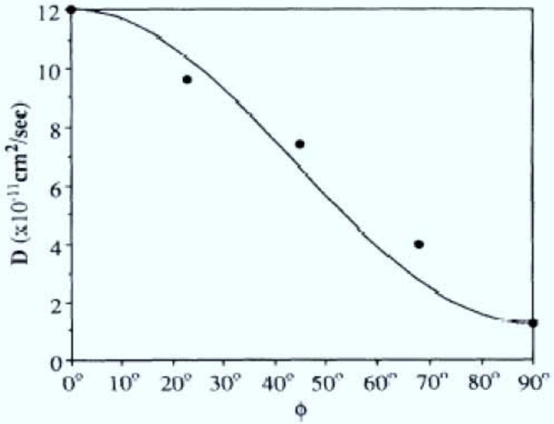
ℓ: jump distance

- At given T the differences in the diff. coeff. can be several orders of magnitude!

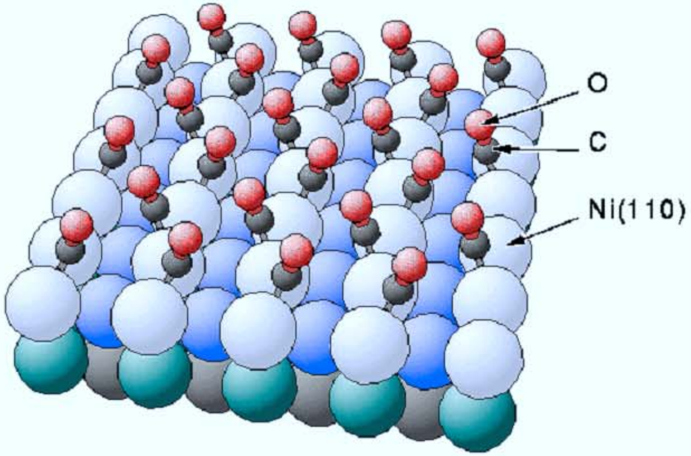
Anisotropy of Surface Diffusion

- **Directional Anisotropy:** the diffusion coefficient depends on the direction at the surface

- Rectangular lattice → directional anisotropy (Xiao et al., PRL 1991)

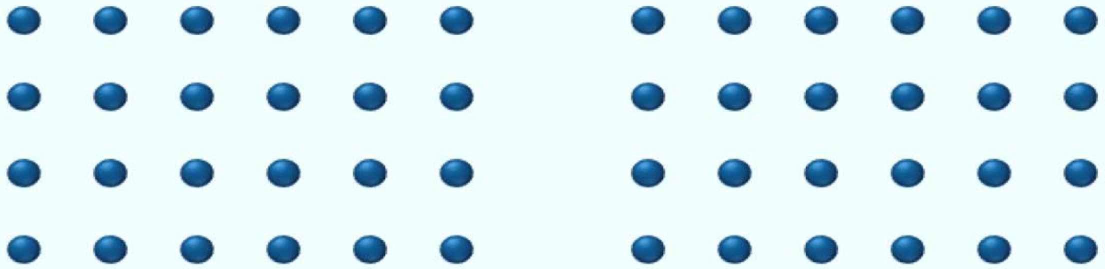


$$D(\varphi) = D_x \cos^2 \varphi + D_y \sin^2 \varphi$$

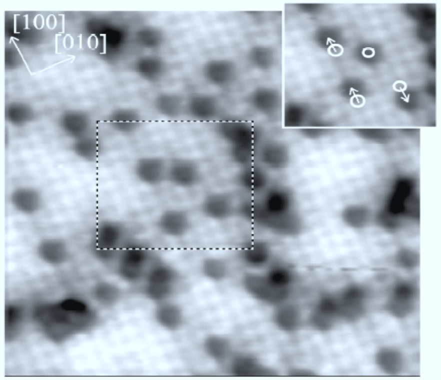


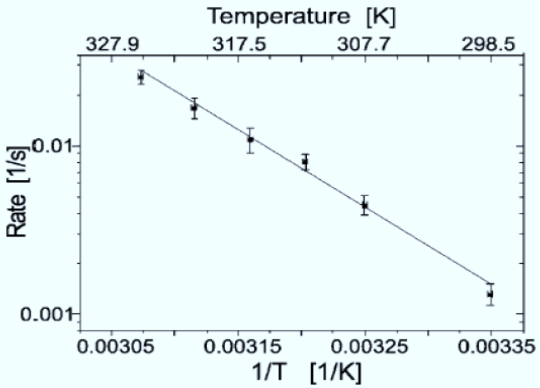
Atomistic Mechanisms

1) Hopping mechanism:



- Example: N adatoms on Fe(100) (Pedersen et al., PRL 2000)

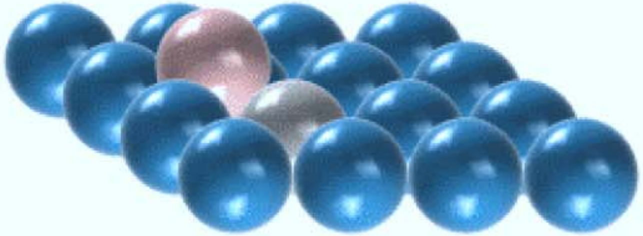


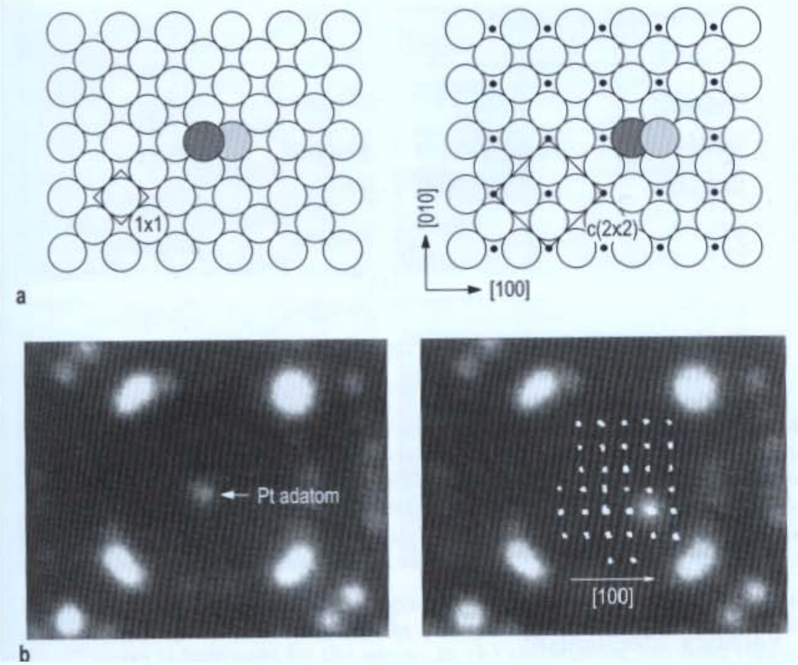


→ Arrhenius law with $\nu \sim 10^{12}\ \mathrm{s}^{-1}$, $E_{diff} = 0.92$ eV

Atomistic Mechanisms

2) Atomic exchange mechanism:





- Example: Pt adatom on Pt(100) (Kellogg, SSR 1994)

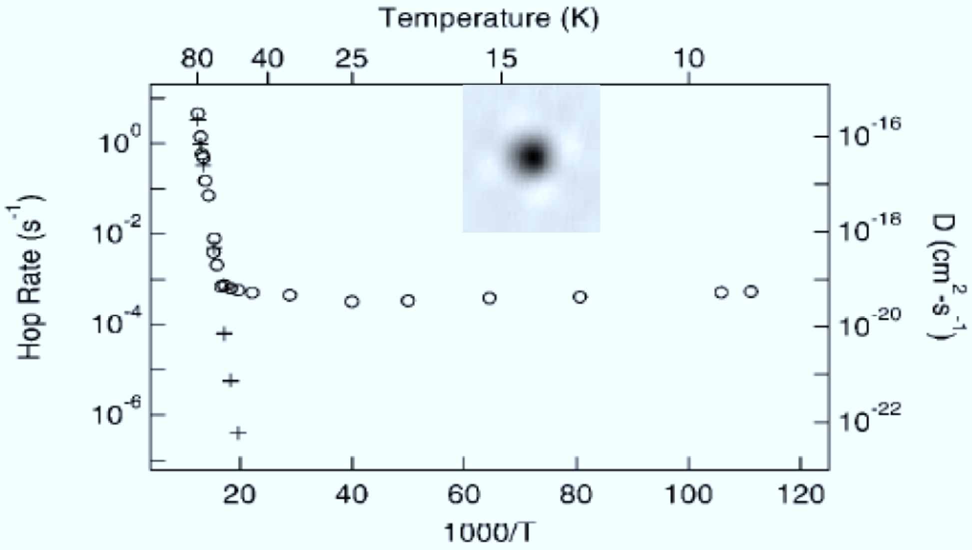
- Observed also on heterosystems [Pt on Ni(110), Ir on Pt(100), Re on Ir(100)]

Atomistic Mechanisms

3) Tunneling mechanism:

- Diffusing particle with small mass
- Low potential barrier against diffusion

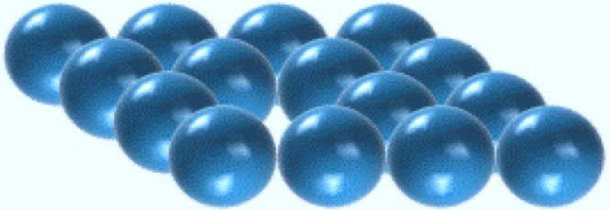
- Example: Hydrogen on Cu(100) (Lauhon & Ho, PRL 2000)



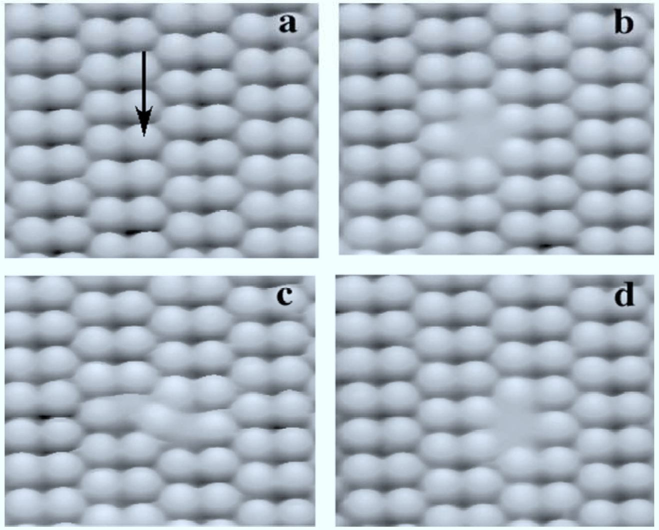
- Above 60 K: Arrhenius law with $\nu \sim 10^{13}\ s^{-1}$, $E_{diff} = 0.20$ eV
- Below 60 K: quantum tunnelling, T independent

Atomistic Mechanisms

4) Vacancy mechanism:



- Example: Ge(111)c(2x8) (Mayne et al., SS 2001)



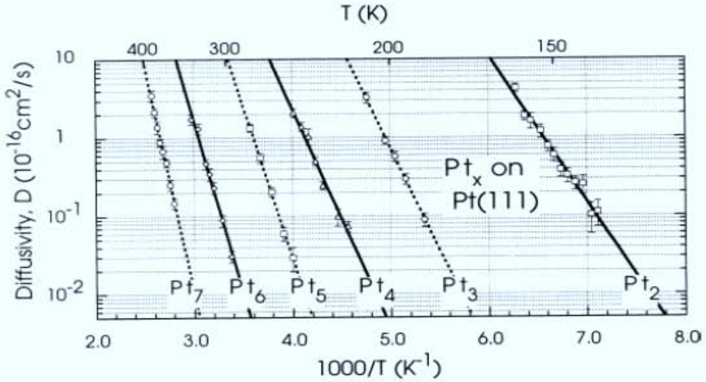
-Vacancy created with the STM tip

- T-activated hopping of neighboring atoms

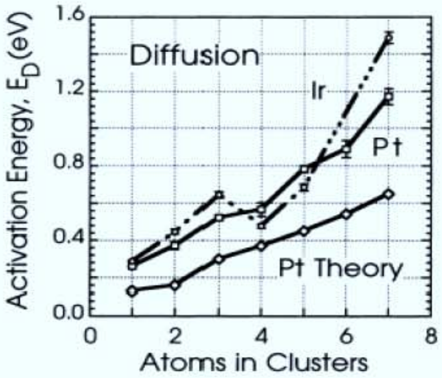
- Heterodiffusion by vacancy-exchange also reported

Cluster Diffusion

- The larger the cluster, the lower its mobility:

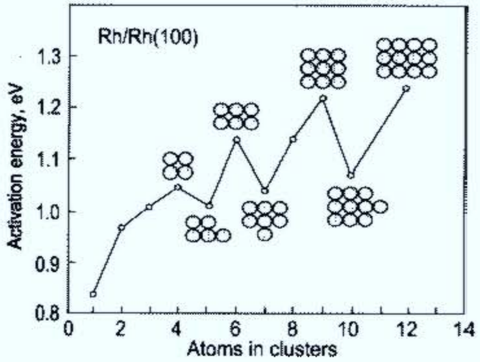


- Activation energy increases with cluster size:



(Kyuno & Ehrlich, SS 1999)

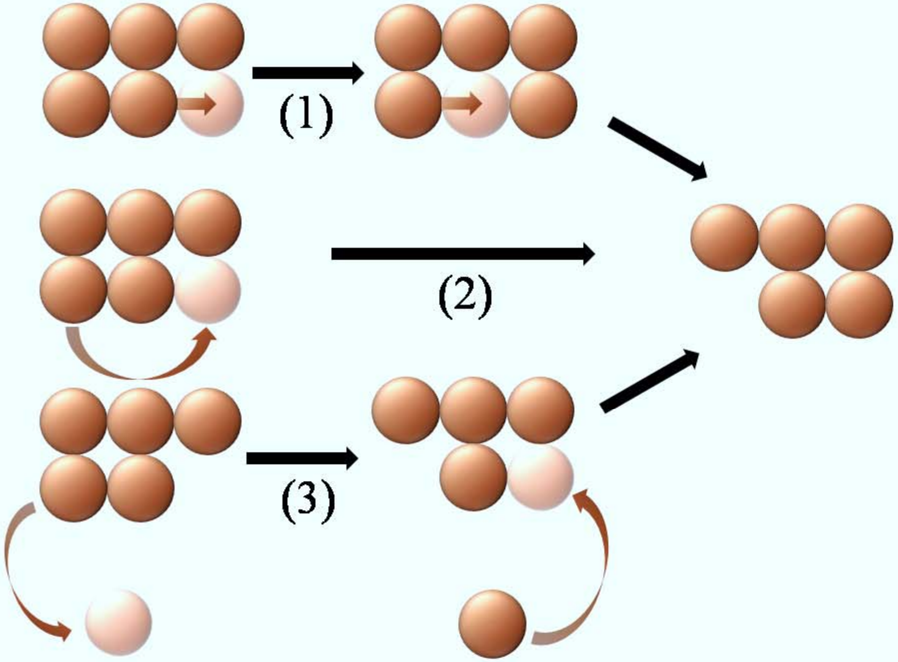
- Compact shapes are less mobile...



(Kellogg, PSS 1996)

Cluster Diffusion

Individual mechanisms:



(1) Sequential displacement

(2) Edge diffusion

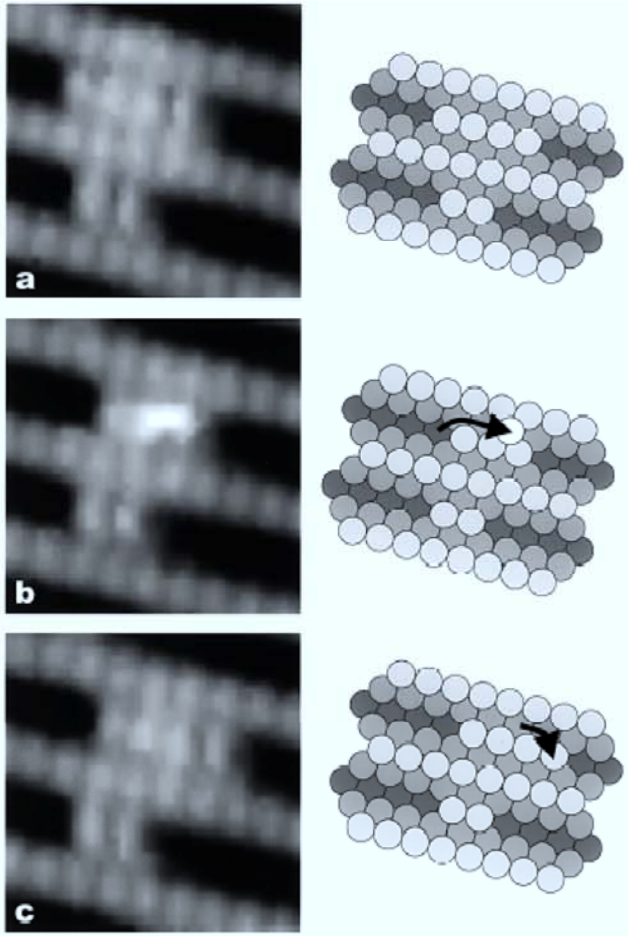
(3) Evaporation-condensation

Cluster Diffusion

Individual mechanisms:

(4) “Leapfrog” mechanism:

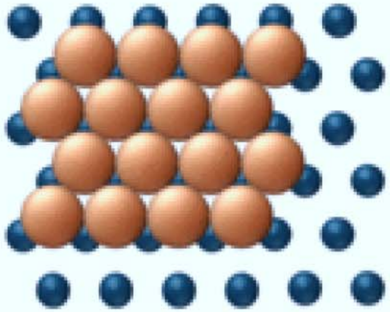
- Example: Pt(110)2x1
(Linderoth et al., PRL 1999)



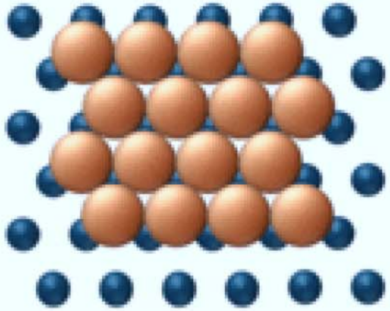
Cluster Diffusion

Concerted mechanisms:

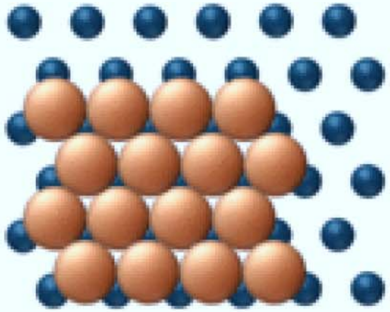
(1) Glide:



(2) Shear:



(3) Reptation:



(4) Dislocation: