Vorlesung 22
Rastertunnelspektroskopie

Übersicht über die Kapitel der Vorlesung

0. Motivation

1. Die Oberfläche

2. Dünne Gase

3. Methoden der Oberflächenphysik

4. Schichtwachstum

5. Oberflächenchemie

6. Elektronische Struktur von Oberflächen

7. Oberflächenmagnetismus

8. Quantennanowissenschaften auf Oberflächen

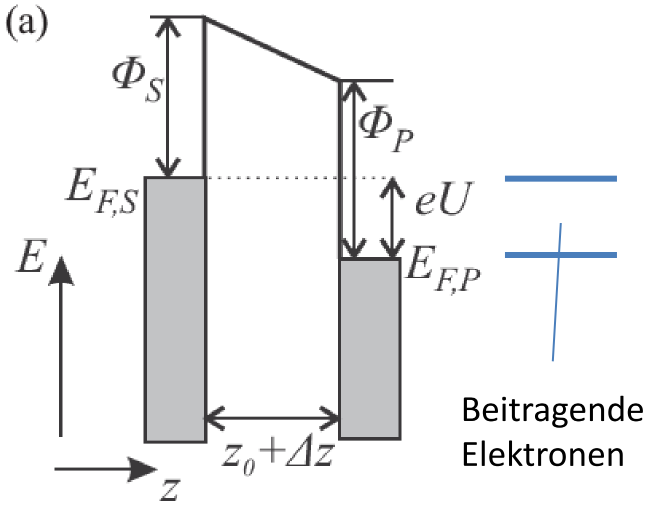
Lernziele

- Rastertunnelspektroskopie
- Oberflächenzustände
- Kondo-Effekt

Quantenmechanik des Tunnelns

- Transmission sieht ähnlich aus für Trapez-Barriere:

$$\mathcal{T}(E,U,\Phi,z_0+\Delta z) = \exp(-2\sqrt{\frac{2m}{\hbar^2}}\sqrt{\Phi + \frac{eU}{2} - E}\,(z_0+\Delta z)).$$



- **Wichtig**: Höhe der Barriere bestimmt durch Austrittsarbeiten

$$\Phi = (\Phi_P + \Phi_S)/2$$

- **Für kleine Tunnelspannungen:**

$$I(\Delta z) = I(z_0)e^{-\alpha \Delta z}\,;\ \alpha = 2\sqrt{2m\Phi}/\hbar = 10{,}25\,\mathrm{nm}^{-1}(\Phi/\mathrm{eV})^{-1/2}.$$

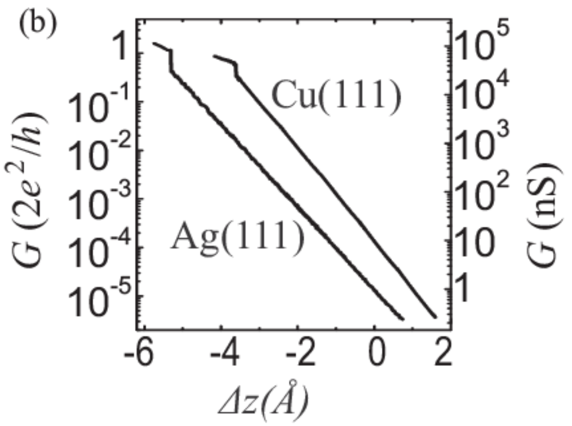


Table 1.1: Work functions and decay constants

Element	Al	Au	Cu	Ir	Ni	Pt	Si	W
ϕ (eV)	4.1	5.4	4.6	5.6	5.2	5.7	4.8	4.8
κ (nm^{-1})	10.3	11.9	10.9	12.1	11.6	12.2	11.2	11.2

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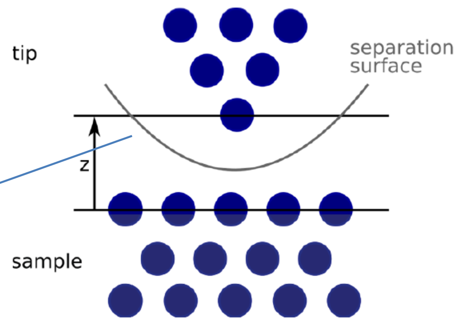
Bardeen Approach

- Vor der Erfindung des STMs
- Elektronentunneln für ein System von planaren Tunnelübergängen, behandelt in einem zeitabhängigen Störungstheorie-Ansatz
- Transfermatrix-Element



Stromdichte-Operator

$$M_{\mu\nu} = -\frac{\hbar^2}{2m}\int [\psi_\mu^* \nabla \psi_\nu - \psi_\nu \nabla \psi_\mu^*] d\boldsymbol{S}$$

Daraus folgt der Tunnelstrom durch Summation

Transfer-Raten nach Fermis goldener Regel

$$I_T(V) = \frac{2\pi e}{\hbar}\sum_{\mu,\nu}[f(E_\mu) - f(E_\nu)]|M_{\mu\nu}|^2 \delta(E_\nu + V - E_\mu) \approx \frac{2\pi}{\hbar} e^2 V \sum_{\mu,\nu} |M_{\mu\nu}|^2 \delta(E_\mu - E_F)\delta(E_\nu - E_F)$$

Low temperatures

Im Limes ergibt dies

$$I_T(V) \propto \int [f_s(\varepsilon - eV) - f_t(\varepsilon)] \rho_S(\varepsilon - eV)\rho_T(\varepsilon) |M(\varepsilon, eV)|^2 \, d\varepsilon$$

Beschreibung des Tunnelprozesses nach Tersoff-Hamann

- Spitze wird durch ein sphärisches Potential beschrieben mit s-artigem Charakter
- Unter dieser Näherungen zeigt ein Konstantstrombild die Fläche gleicher Elektronendichte.

Zustandsdichte Spitze

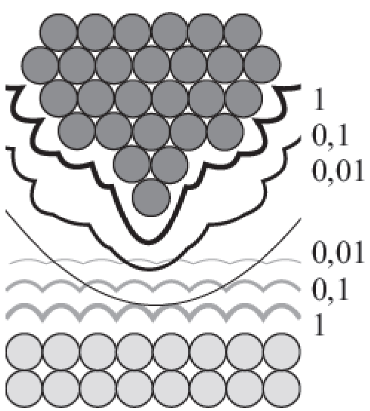
$$I(x,y,z,U) \propto \int_{-\infty}^{\infty} D_S(E-eU)\rho(x,y,z,E)(f(E-eU,T_S)-f(E,T_P)dE$$

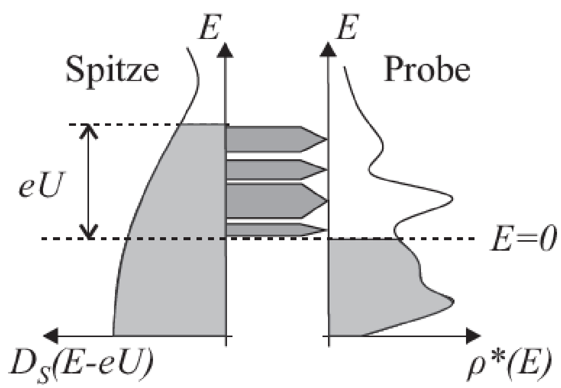
Für tiefe Temperaturen: $T_P = T_S = 0$

Zustandsdichte Probe

$$I(x,y,z,U) \propto \int_0^{eU} D_S(E-eU)\rho^*(x,y,E)\mathcal{T}(E,U,z)dE.$$

Transmissions funktion





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Rastertunnelspektroskopie nach Tersoff-Hamann

- Rastertunnelspektroskopie: lokale elektronische Struktur der Oberfläche

$$I(x,y,z,U) \propto \int_0^{eU} D_S(E-eU)\rho^*(x,y,E)\mathcal{T}(E,U,z)dE.$$

⇓

Zustandsdichte der Probe

$$\frac{\partial}{\partial U}I(x,y,z_0,U) \propto e\mathcal{T}(eU,U,z_0)D_S(0)\rho^*(x,y,eU)$$
$$+\int_0^{eU}\rho^*(x,y,E)\mathcal{T}(E,U,z_0)\frac{\partial}{\partial U}D_S(E-eU)dE$$
$$+\int_0^{eU}\rho^*(x,y,E)D_S(E-eU)\frac{\partial}{\partial U}\mathcal{T}(E,U,z_0)dE. \quad (6.4)$$

Gute Spitze?

Hintergrund

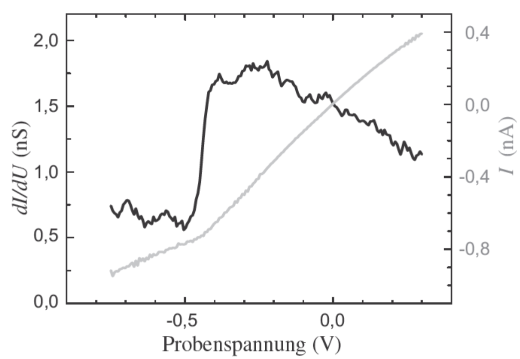

Abb. 6.7: *I(U)-Kennlinie (grau, rechte Skala) und STS-Spektrum (schwarz, linke Skala) bei $T = 6$ K auf einer ausgedehnten Terrasse eines Cu(111)-Kristalls aufgenommen. Der starke Anstieg des dI/dU-Signals bei $-0{,}44$ V zeigt das Bandminimum des Oberflächenzustands an.*

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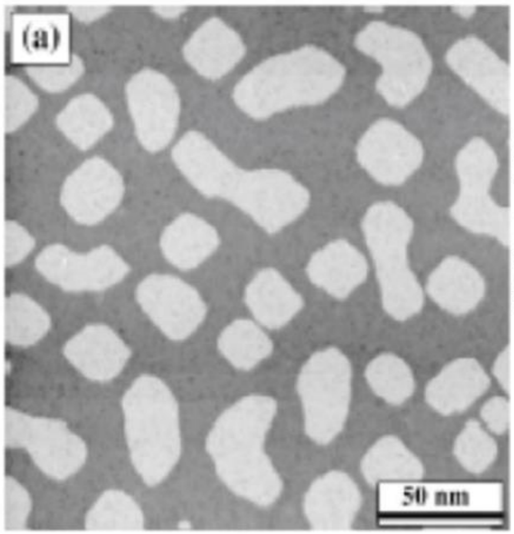
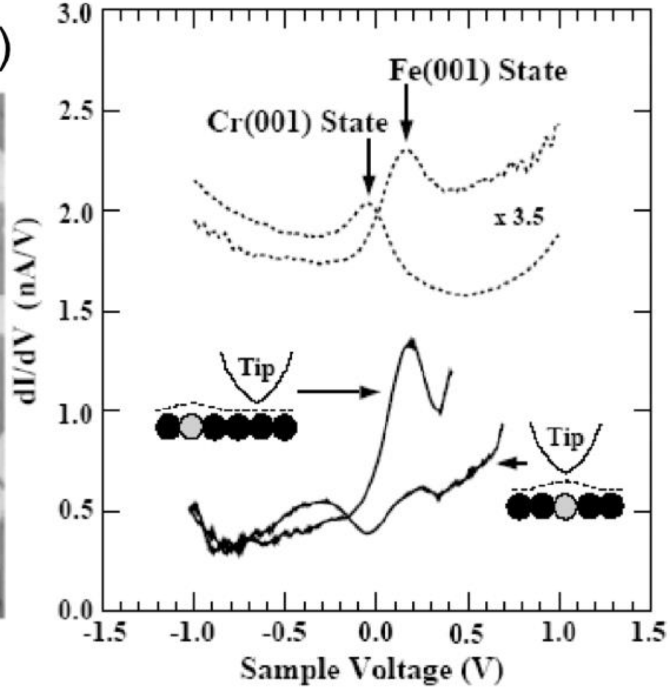
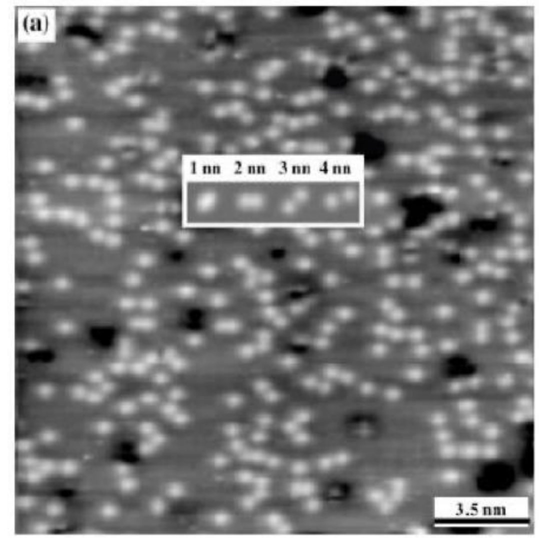
- **“chemische” Auflösung**
- **Legierungsbildung an der Cr-Fe(001)-Grenzfläche**

Topographie Cr/Fe(001)





dI/dV bei -0.3 V

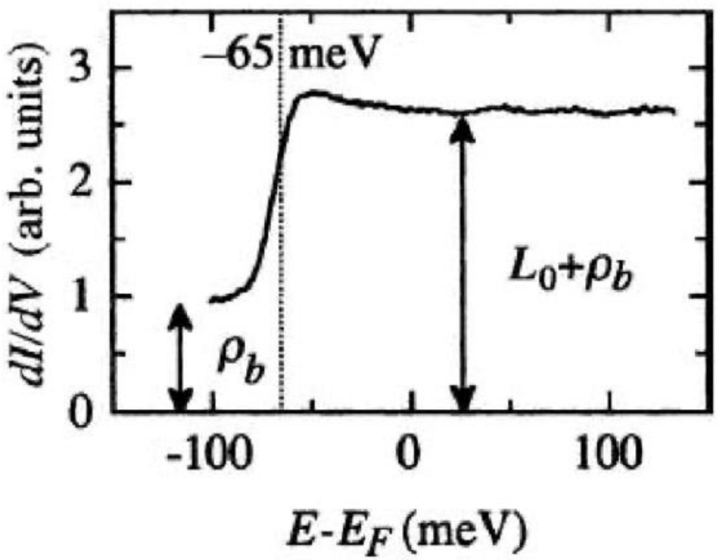


- Cr und Fe haben ihre spezifischen lokalen Zustandsdichten die einem elektronischen „Fingerabdruck“ gleich kommen.
- Lokale Messung von dI/dV ermöglicht atomare chemische Identifikation.

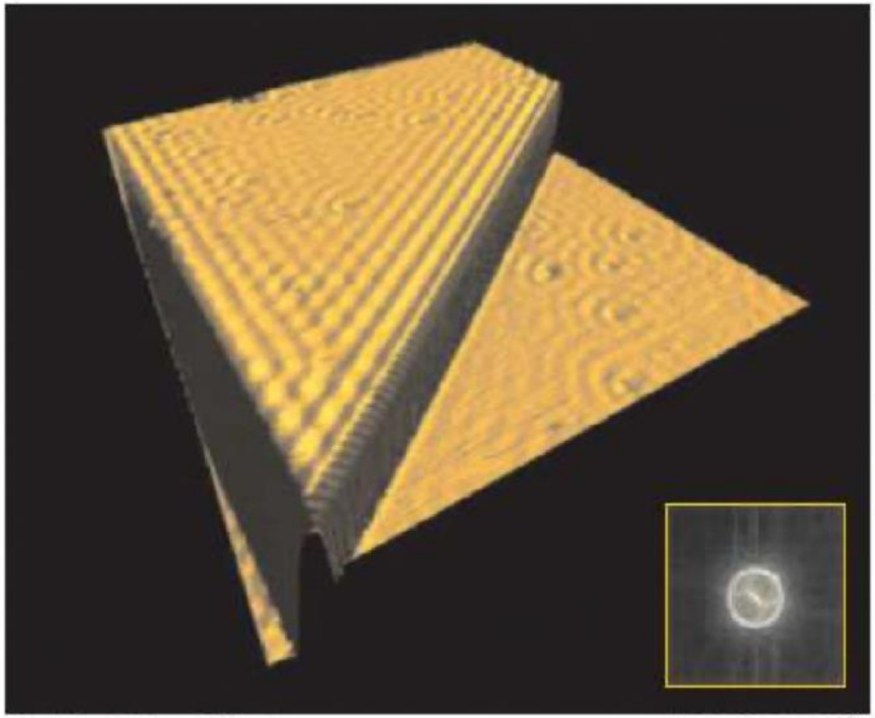
https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.76.4175

Der Oberflächenzustand von Ag(111)

Tunnelspektrum



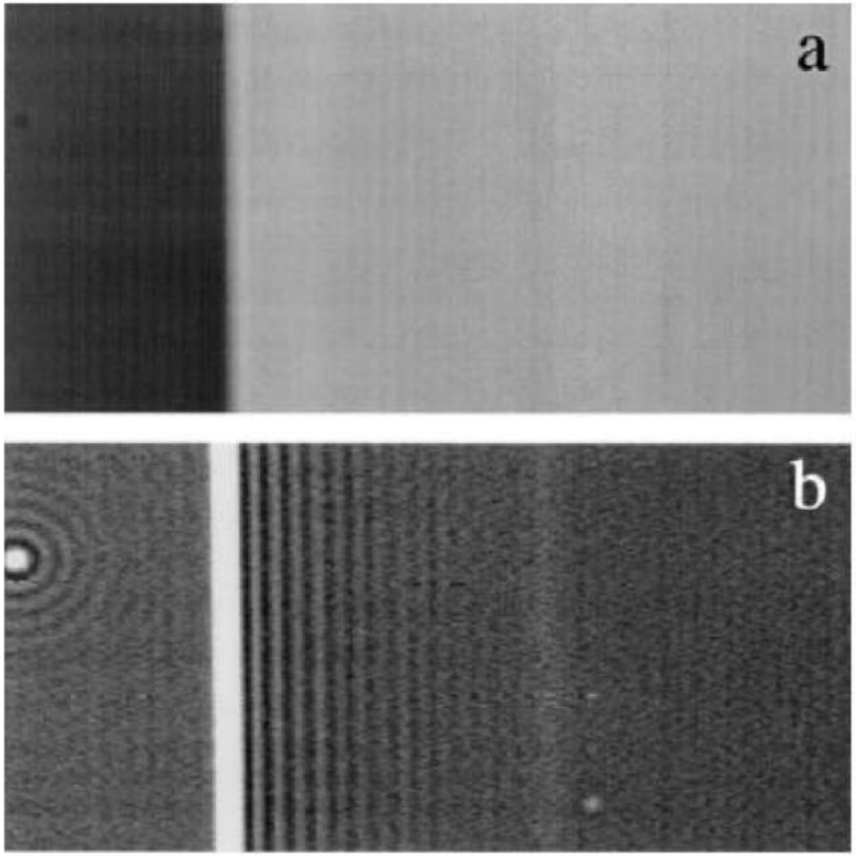
Topographie

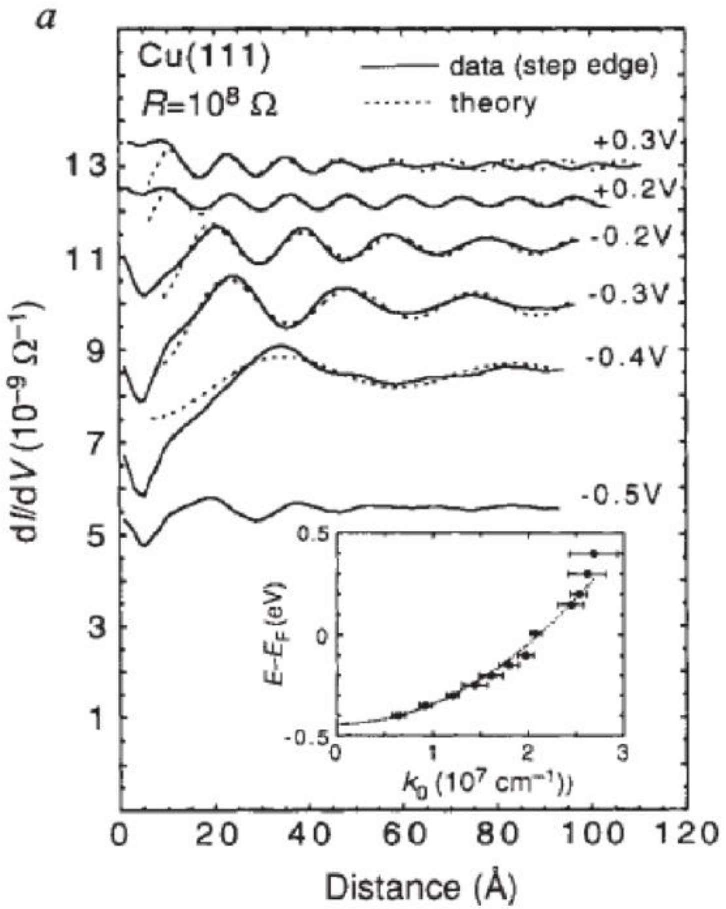


$V_t = 13$ mV, $I_t = 0.32$ nA 1000 X 1000 Å^2

- Oberflächenzustand erzeugt Stufe in der differentiellen Leitfähigkeit, da die Zustandsdichte konstant ist.
- Der Oberflächenzustand wird an Stufen und Defekten gestreut.

Der Oberflächenzustand von Cu(111)



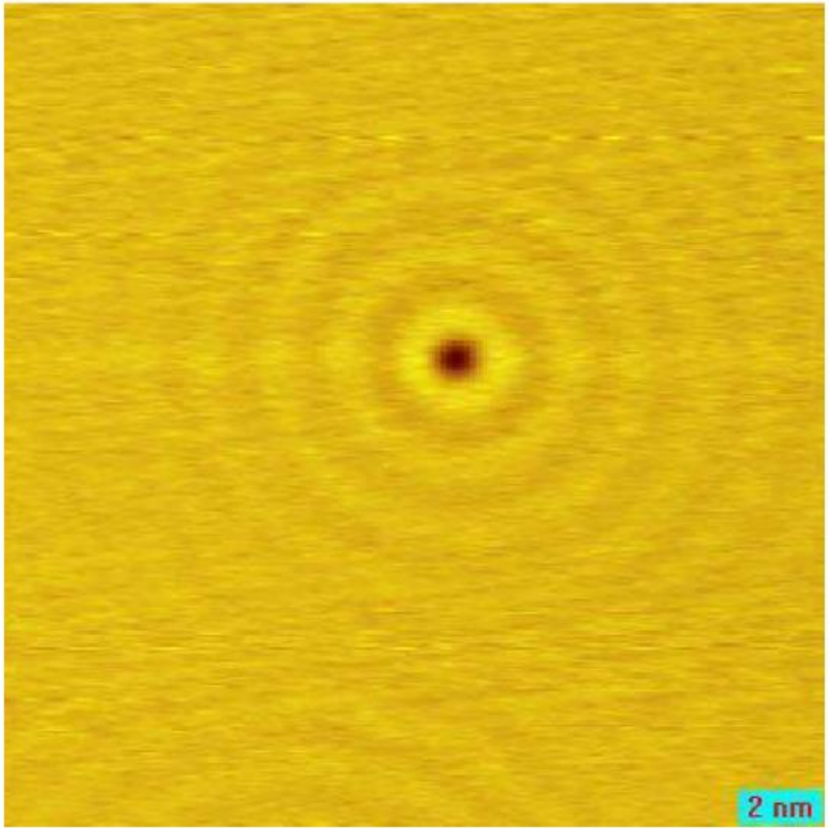


Effektive Masse $m^*/m_0 = 0.38$, Bandkante -0.4 eV

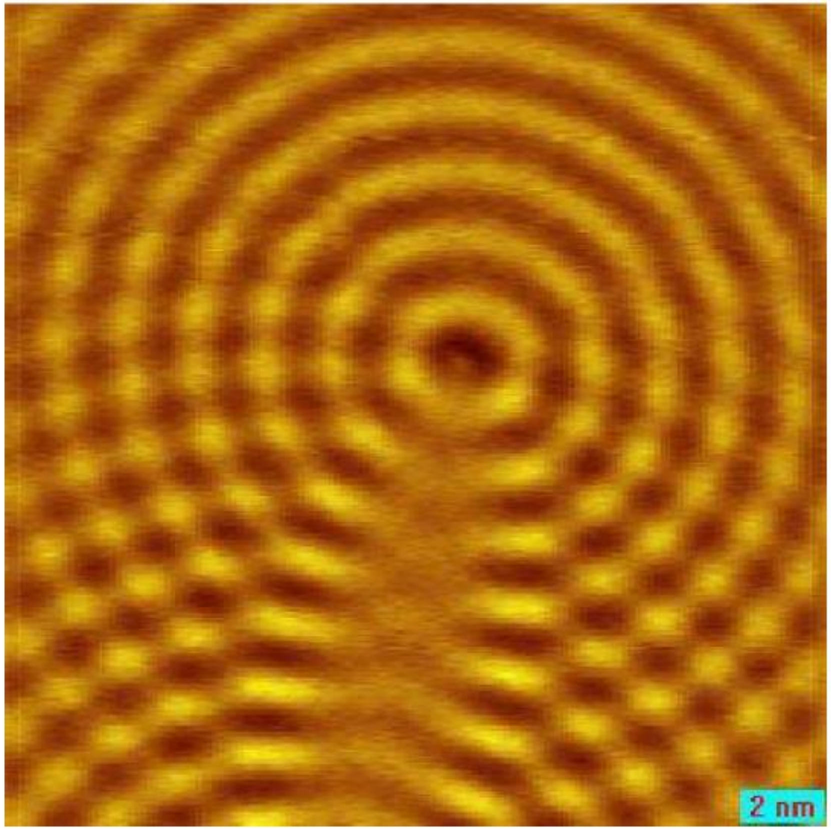
https://www.nature.com/articles/363524a0

Der Oberflächenzustand von Cu(111)

Topographie

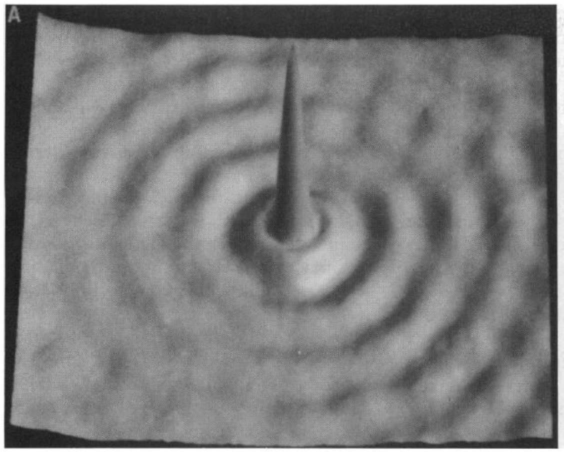


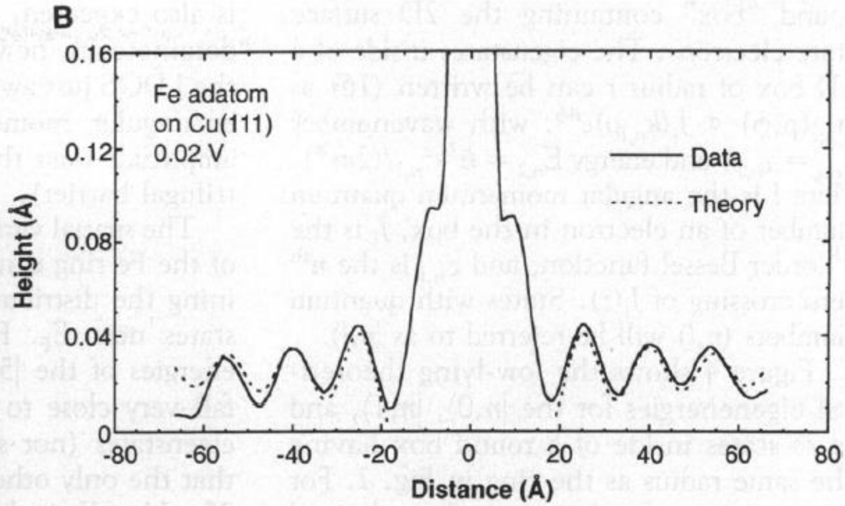
dI/dV bei 50mV



Streuung an einzelnen Defekten (hier CO) führt zu stehenden Wellen in der Topographie und in der lokalen Zustandsdichte.

Fe atom on Cu(111)





- The local density of states (LDOS) at EF surrounding the adatom is marked by a circular standing wave pattern caused by the interference of incident and scattered surface state electrons

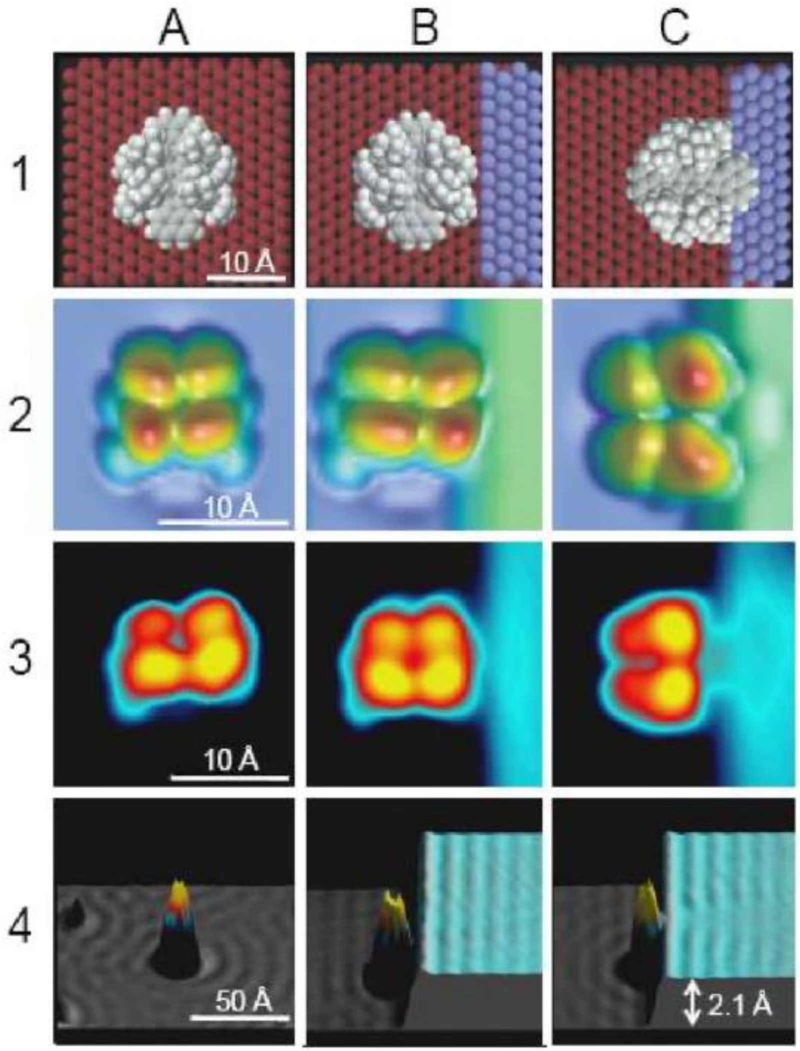
$$\Delta \mathrm{LDOS}(\rho) \propto \frac{1}{k\rho}\left(\cos^2\left(k\rho - \frac{\pi}{4} + \delta_0\right) - \cos^2\left(k\rho - \frac{\pi}{4}\right)\right)$$

distance

Phase shift

https://www.science.org/doi/pdf/10.1126/science.262.5131.218

Kontaktierung des 2D Elektronengases durch ein Lander-Molekül



Wenn Landermolekül eine Stufe einer Cu(111) Oberfläche mit dem organischen Ringsystem berührt (C), kommt es zu Streuung.

Das Molekül kontaktiert das 2D Elektronengas.

FU Berlin

https://journals.aps.org/prl/pdf/10.1103/PhysRevLett.91.036601

Quantum Corral

- A circular corral of radius 71.3 A was constructed in this way out of 48 iron adatoms.

→ Manipulation von Streuern auf der Oberfläche mit 2DEG ermöglicht Experimente zur fundamentalen Quantenmechanik

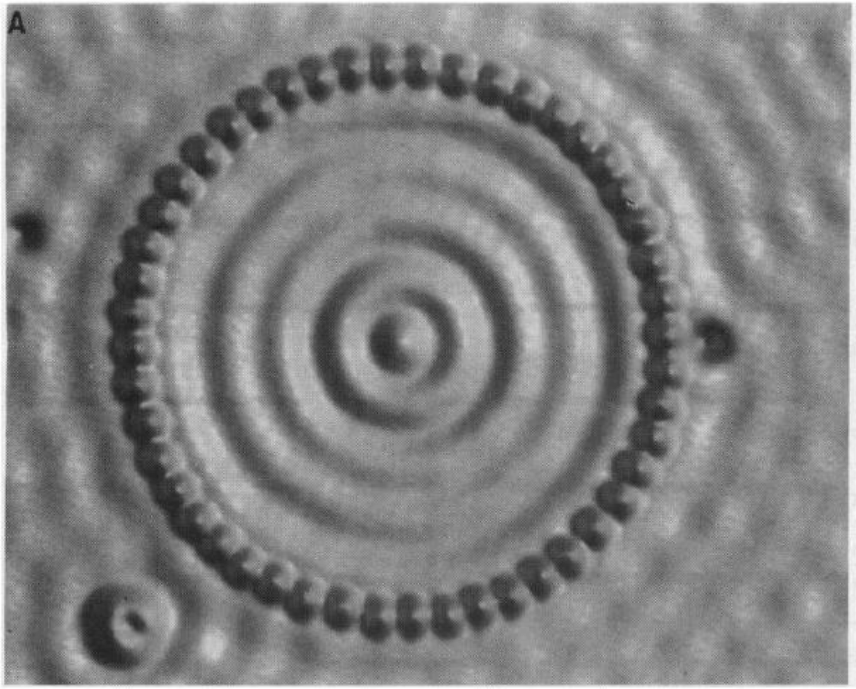
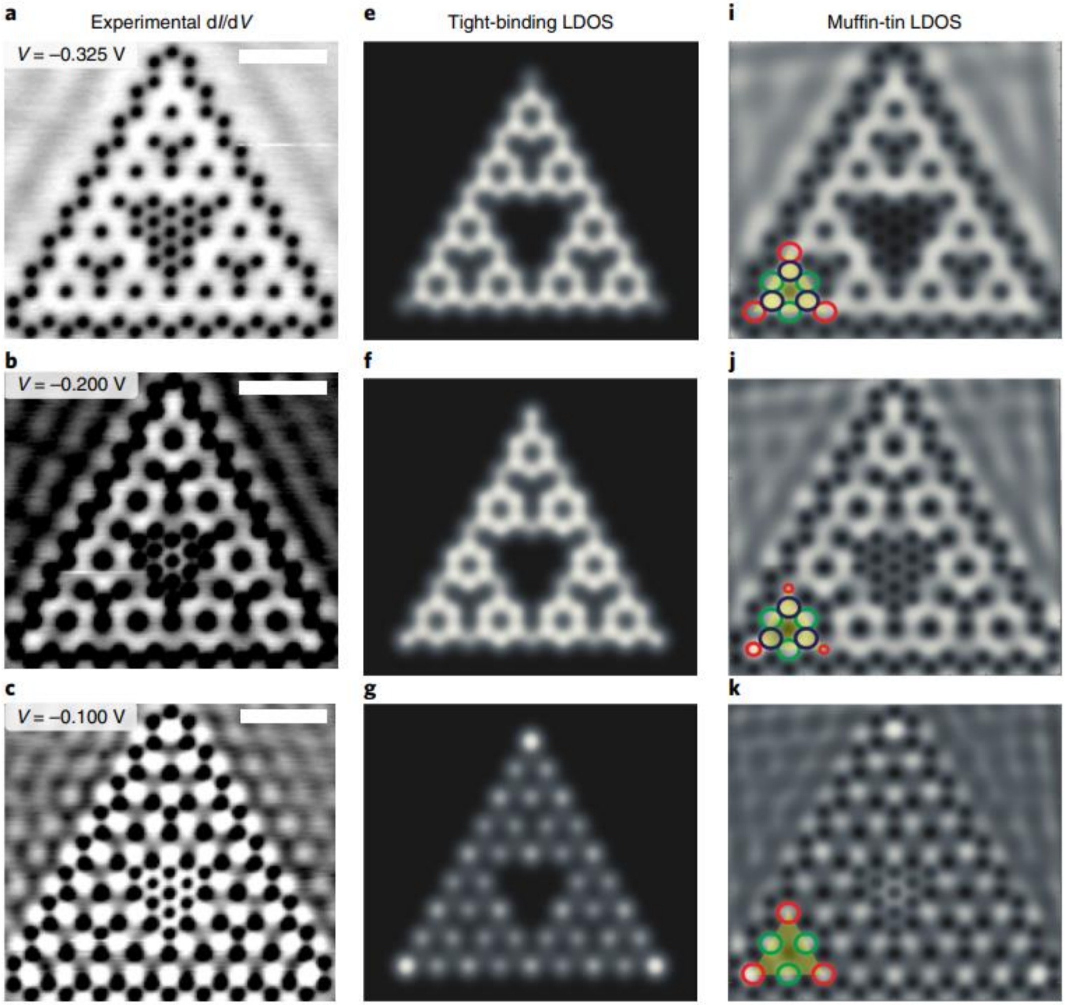


Fig. 2. Spatial image of the eigenstates of a quantum corral. (**A**) 48-atom Fe ring constructed on the Cu(111) surface (V = 0.01 volt, I = 1.0 nA). Average diameter of ring (atom center to atom center) is 142.6 Å. The ring encloses a

CO molecules on a Cu (111)

- Electronic quantum fractals can be artificially created by atomic manipulation in a scanning tunnelling microscope.
- Sierpiński triangle with Hausdorff dimension log(3)/log(2)=1.58



https://www.nature.com/articles/s41567-018-0328-0

Seeing the Fermi Surface in Real Space by Nanoscale Electron Focusing

Alexander Weismann,[1,2] Martin Wenderoth,[1*] Samir Lounis,[3] Peter Zahn,[4] Norbert Quaas,[1] Rainer G. Ulbrich,[1] Peter H. Dederichs,[3] Stefan Blügel[3]

- Auch im Volumen lassen sich Streuer identifizieren

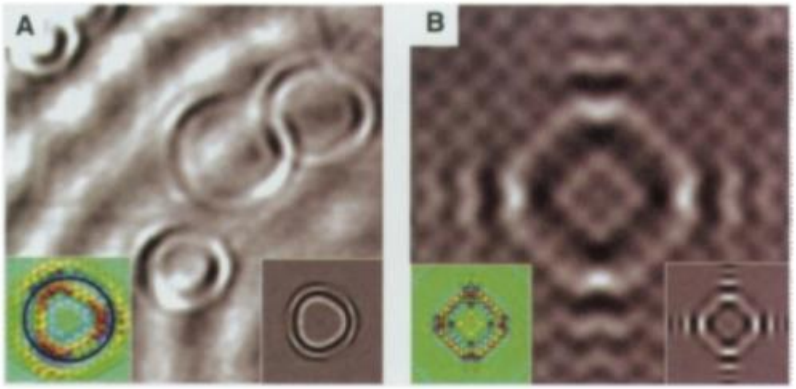


Fig. 1. STM topographies of (**A**) four Co-Atoms below the Cu(111) surface (9 by 9 nm, –80 mV, 1 nA) and (**B**) one Co Atom below the Cu(100) surface (3.5 by 3.5 nm, 10 mV, 2 nA). The right insets show (4 by 4 nm) calculated LDOS using Eq. 2, whereas the left insets refer to DFT calculations.

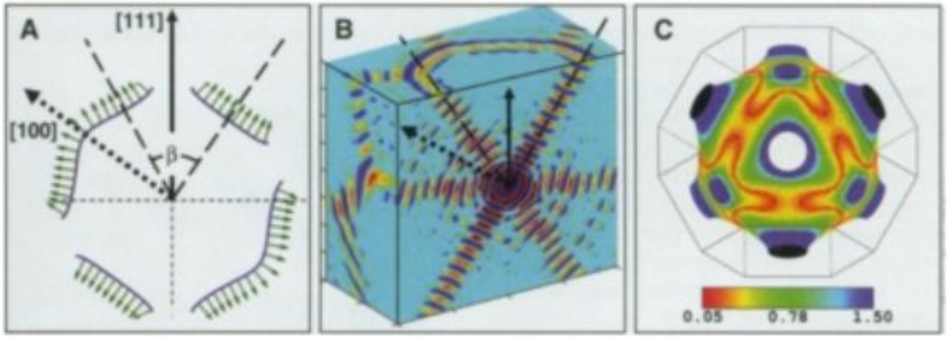


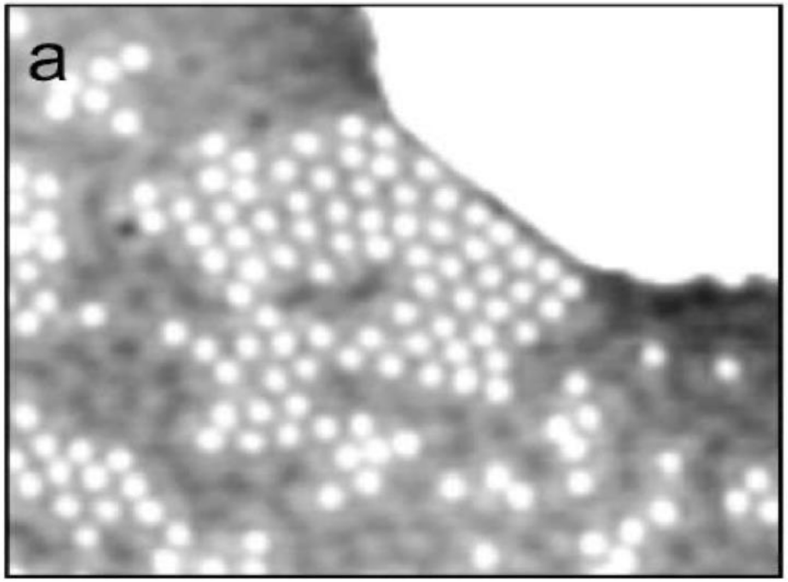
Fig. 3. (**A**) Cross section of the Cu Fermi surface showing areas of reduced curvature and band-gaps in [111] directions. (**B**) Corresponding propagator [$-\text{Im}G_0(\mathbf{x},\mathbf{x}',\varepsilon_F)$] with strong electron focusing onto hollow-conelike beams around [111]. (**C**) The Gaussian curvature of the Cu Fermi surface is represented with color. The drawing plane is oriented perpendicular to the [111] direction. Small curvatures represented in red lead to high amplitudes of the LDOS oscillations.

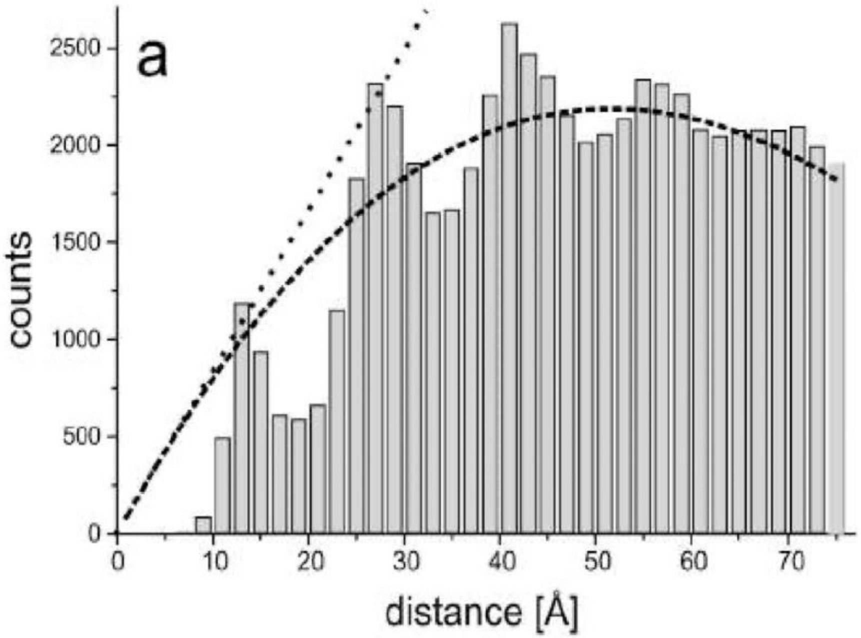
https://www.science.org/doi/10.1126/science.1168738

- Oberflächenzustände können Adsorption beeinflussen

→ Substratvermittelte langreichweitige oszillierende Wechselwirkung zwischen Adatomen

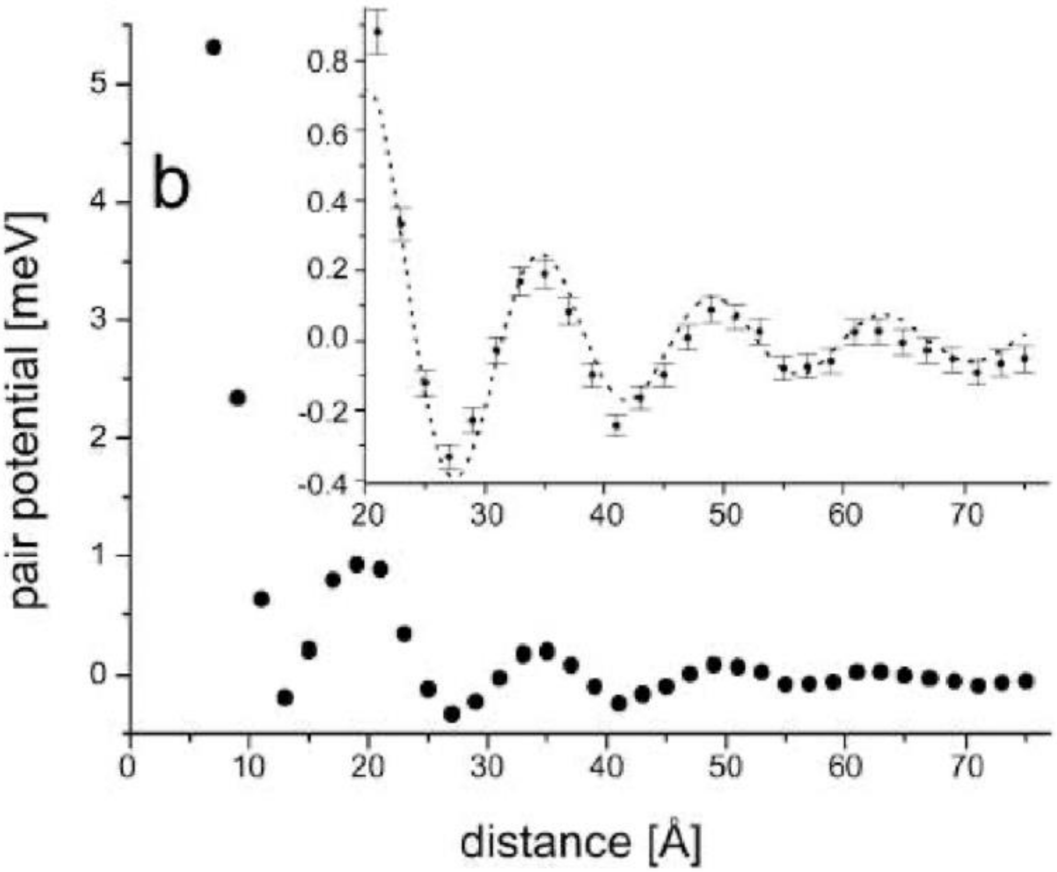
Cu auf Cu(111)

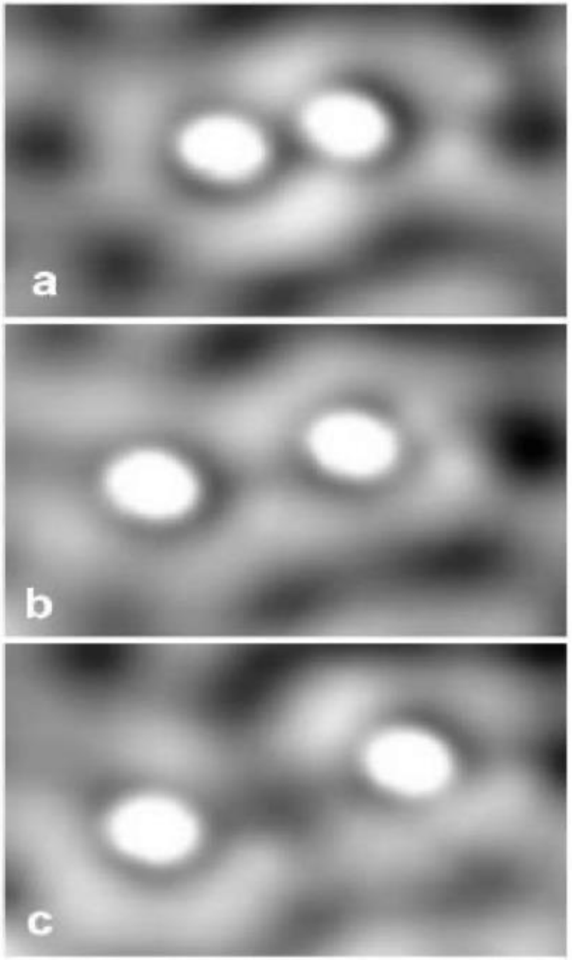




https://journals.aps.org/prl/pdf/10.1103/PhysRevLett.85.2981

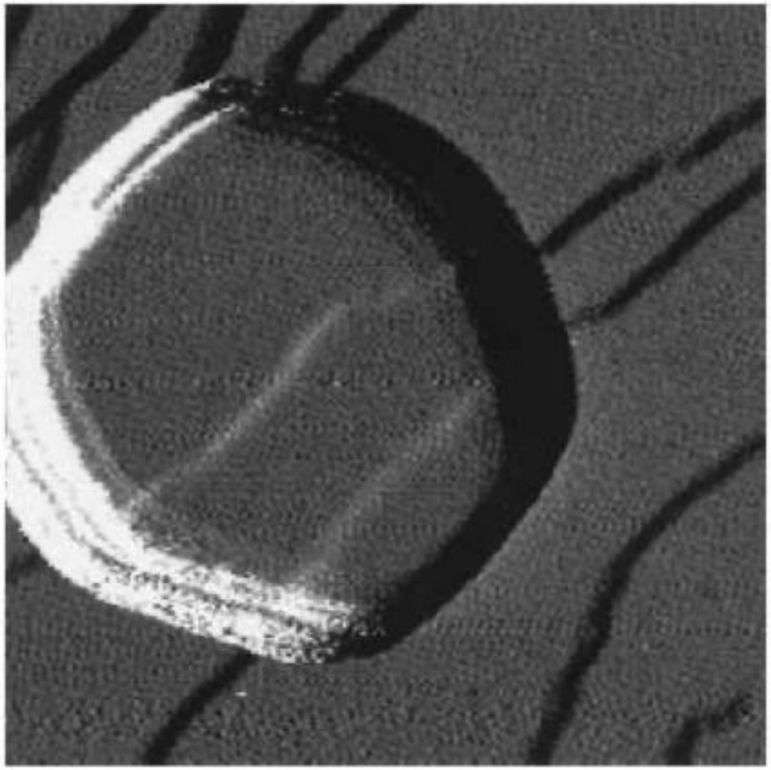
Stehende Wellen des Oberflächenzustandes



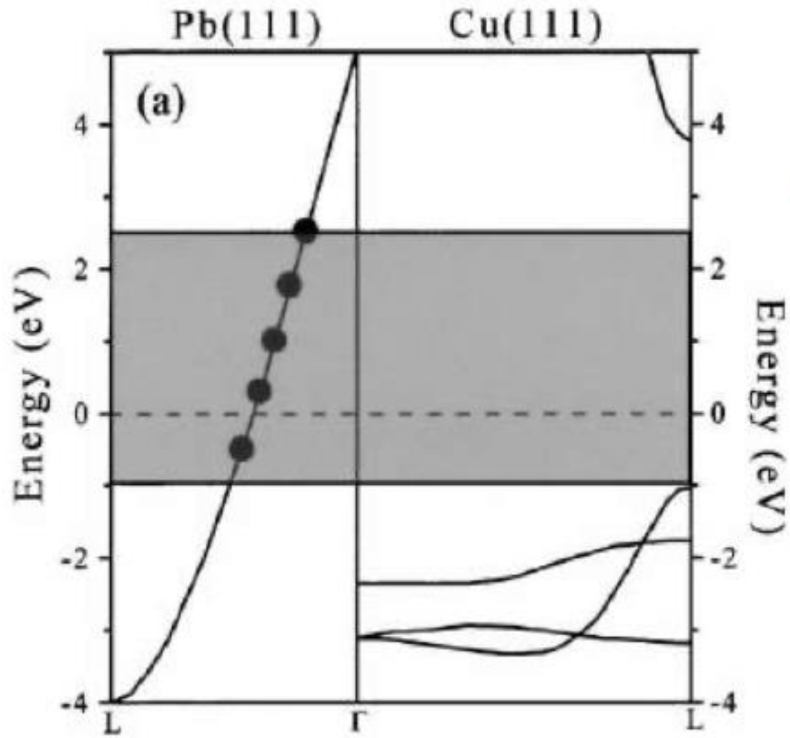


Pb Schichten auf Cu(111)

Pb Inseln auf Cu(111)



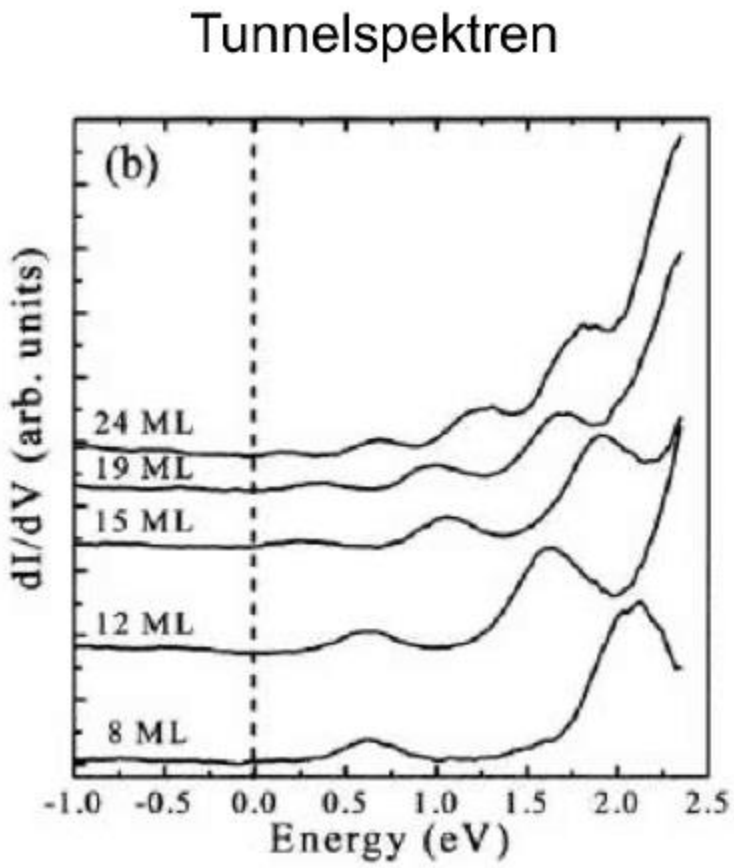
Bandstruktur senkrecht zur Oberfläche

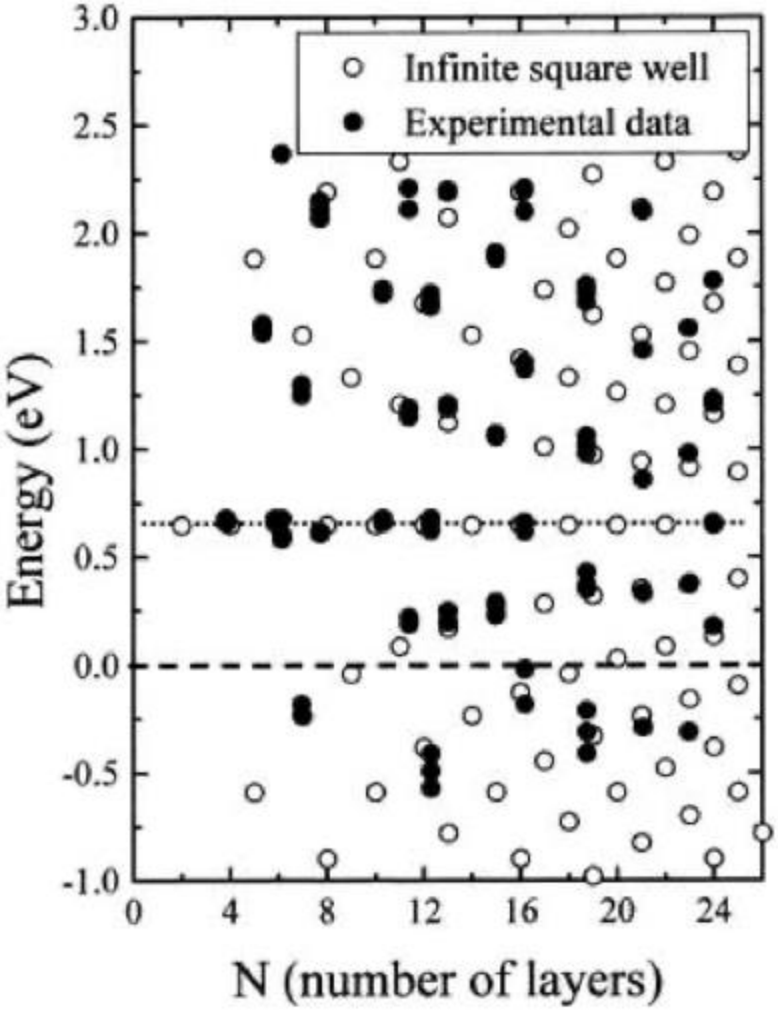


Elektronen in Pb Schicht sind in einem Quantentrog senkrecht zur Oberfläche eingeschlossen.

https://journals.aps.org/prb/abstract/10.1103/PhysRevB.66.115401

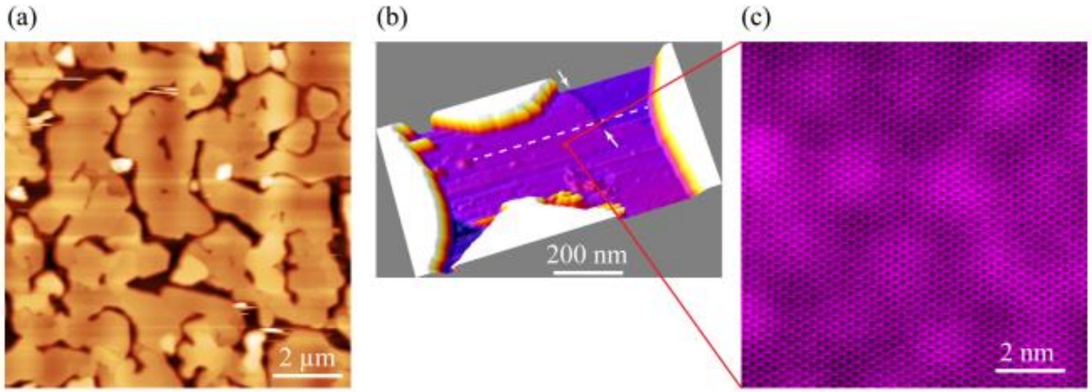
Die elektronische Struktur Pb auf Cu(111)





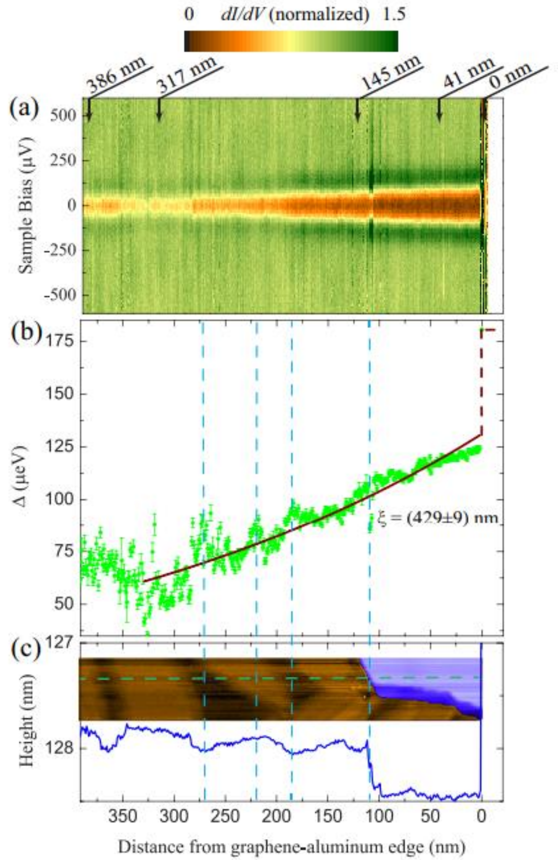
https://journals.aps.org/prb/abstract/10.1103/PhysRevB.66.115401

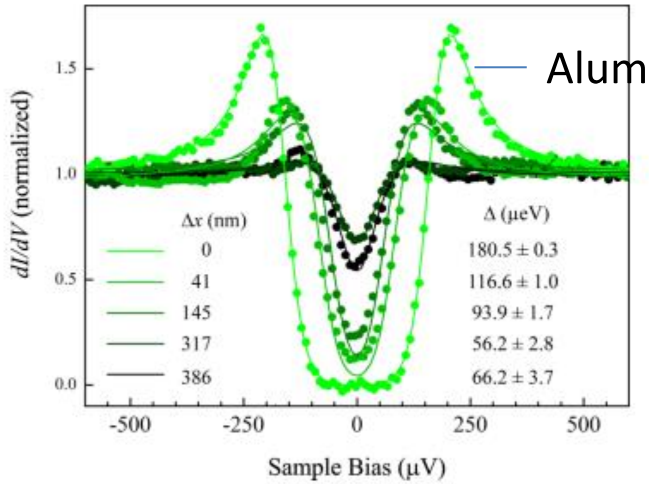
- **More Examples**: Superconducting gap and Proximity effect:



Aluminum on graphene

Ortsabhängige STS
→ Proximity effect





Aluminum SC gap

https://journals.aps.org/prb/pdf/10.1103/PhysRevB.93.045406

Karlsruhe Institute of Technology

- Examples: Single magnetic impurities on surfaces

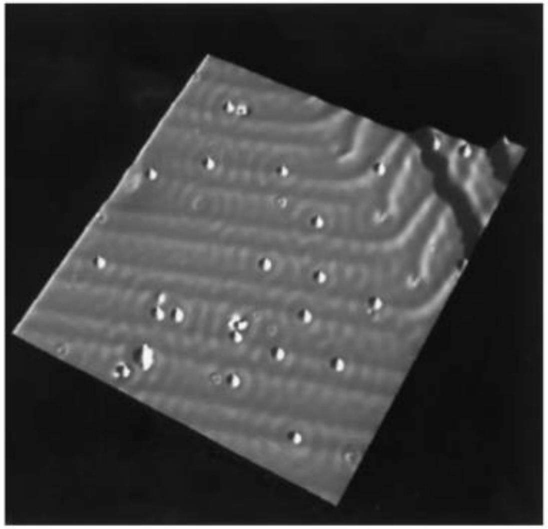
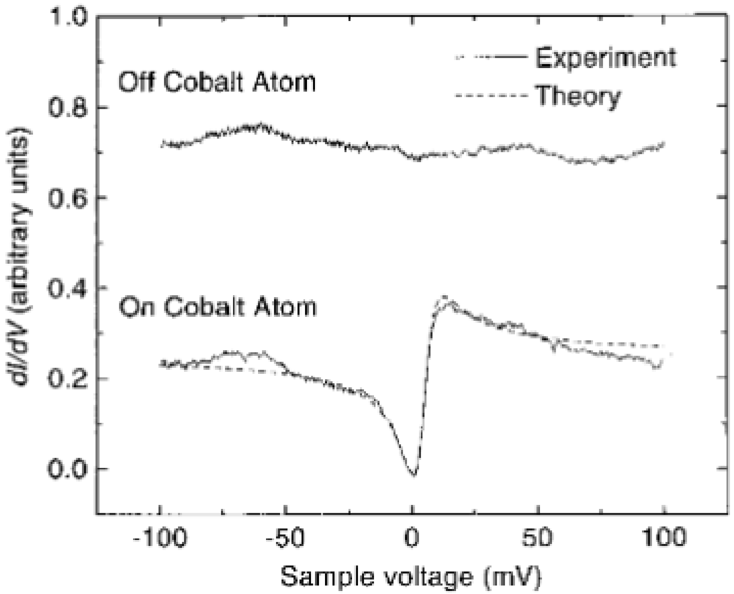


Fig. 1. Constant-current image (400 Å by 400 Å) of the Au(111) surface after deposition of 0.001 monolayer of Co at 4 K (tunnel parameters: $I = 0.5$ nA, $V = 0.1$ V). Approximately 22 Co atoms can be seen nestled among the ridges of the Au(111) herringbone reconstruction.



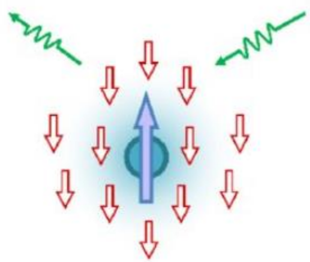
Kondo-Effect: - magnetc impurity in a conducting host at low temperatures
- first discovered in transport experiments

https://www.science.org/doi/epdf/10.1126/science.280.5363.567

- Impurity spectral function A(ω) of a single-level Anderson impurity model

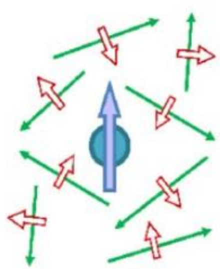
$$H=\sum_{k,\sigma}\epsilon_k c^\dagger_{k\sigma}c_{k\sigma}+\sum_{\sigma}\epsilon_d d^\dagger_\sigma d_\sigma+U d^\dagger_\uparrow d_\uparrow d^\dagger_\downarrow d_\downarrow+\sum_{k,\sigma}V_k\left(d^\dagger_\sigma c_{k\sigma}+c^\dagger_{k\sigma}d_\sigma\right),$$

cond. e — impurity — on–site Coulomb repulsion — hybridization



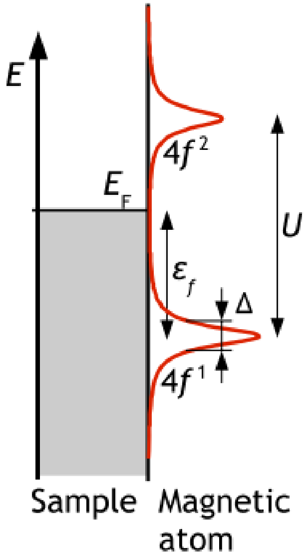
- Below Tκ: Kondo state is formed with the local spin moment at the impurity, screened by the spins of conduction electrons in the leads.

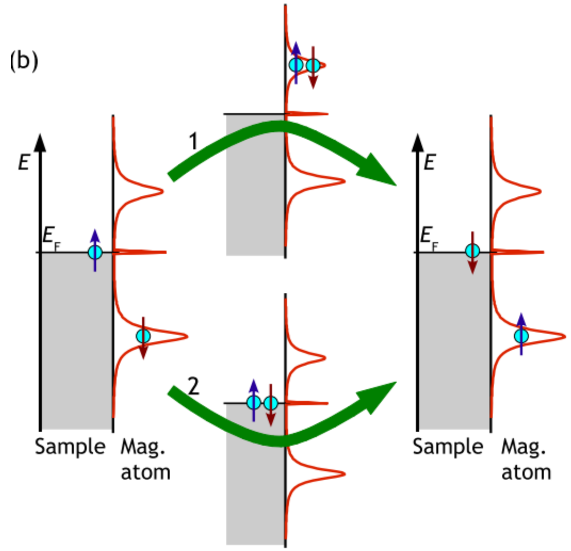
K

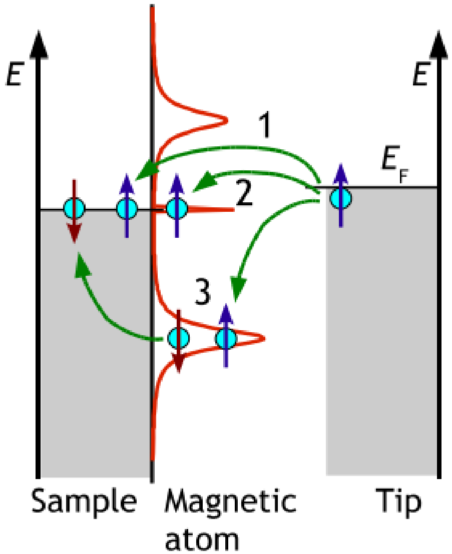


- Above Tκ: enhanced thermal motion of conduction electrons destroys the Kondo state.

Intermediate step







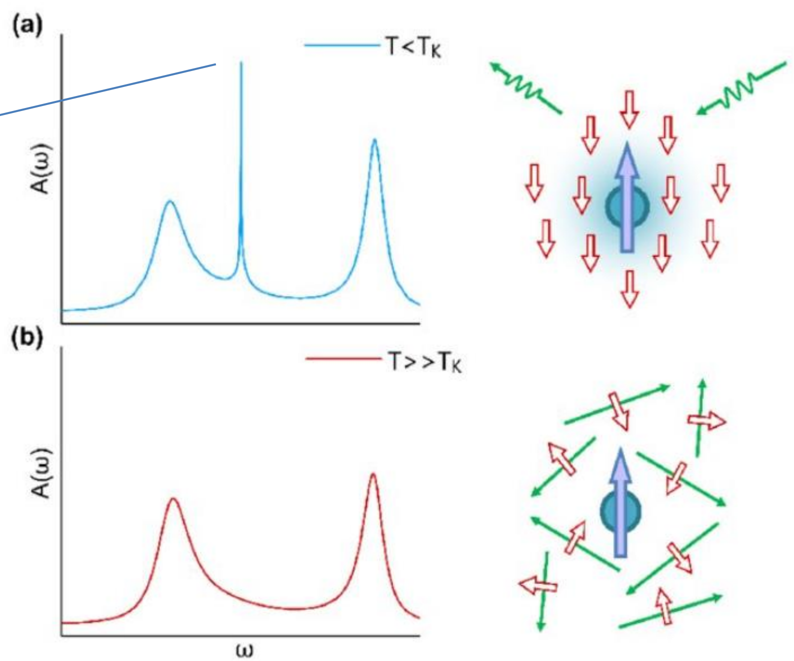
- energy-dependent DOS of a single magnetic adatom on a metal surface
- spin of the singly occupied 4f state can be flipped by a bulk electron of opposite spin via 2 processes
- Different tunnel paths of a probing tip

Kondo resonance width:

$$\Gamma = k_B T_K \simeq \sqrt{2\Delta \frac{U}{\pi}} \exp\left[-\frac{\pi}{2\Delta}\left(\left|\frac{1}{\epsilon_f}\right| + \left|\frac{1}{\epsilon_f + U}\right|\right)^{-1}\right]$$

https://iopscience.iop.org/article/10.1088/0953-8984/21/5/053001/pdf

Kondo resonance peak



- Below T_K: Kondo state is formed with the local spin moment at the impurity, screened by the spins of conduction electrons in the leads.

- Above T_K: enhanced thermal motion of conduction electrons destroys the Kondo state.

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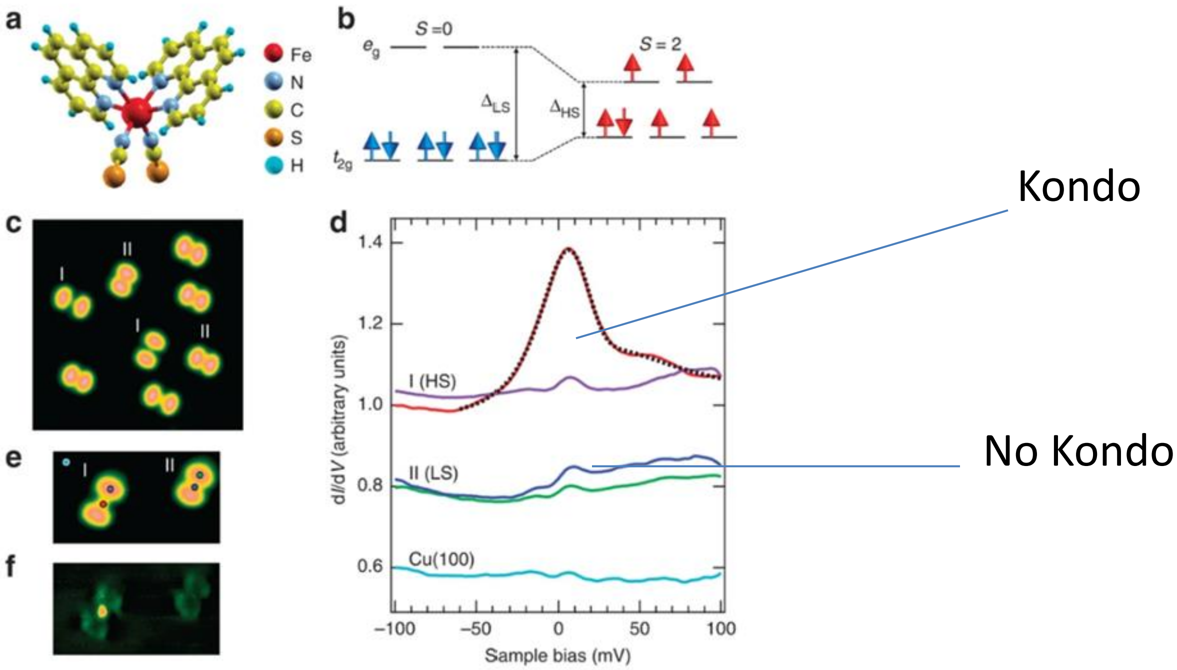
Robust spin crossover and memristance across a single molecule

Toshio Miyamachi, Manuel Gruber, Vincent Davesne, Martin Bowen, Samy Boukari, Loïc Joly, Fabrice Scheurer, Guillaume Rogez, Toyo Kazu Yamada, Philippe Ohresser, Eric Beaurepaire & Wulf Wulfhekel

Nature Communications **3**, Article number: 938 (2012) | Cite this article

Figure 1: SCO Fe-phen molecules on bare Cu(100).



Literatur

- Oberflächenzustände: Ibach, S. 394-407
  Fauster S. 26-36
- Rastertunnelspektroskopie: Fauster, S. 135-137