STM Imaging of Semiconductors, Metals & Molecules

- Semiconductors

Si(100) 2x1 image

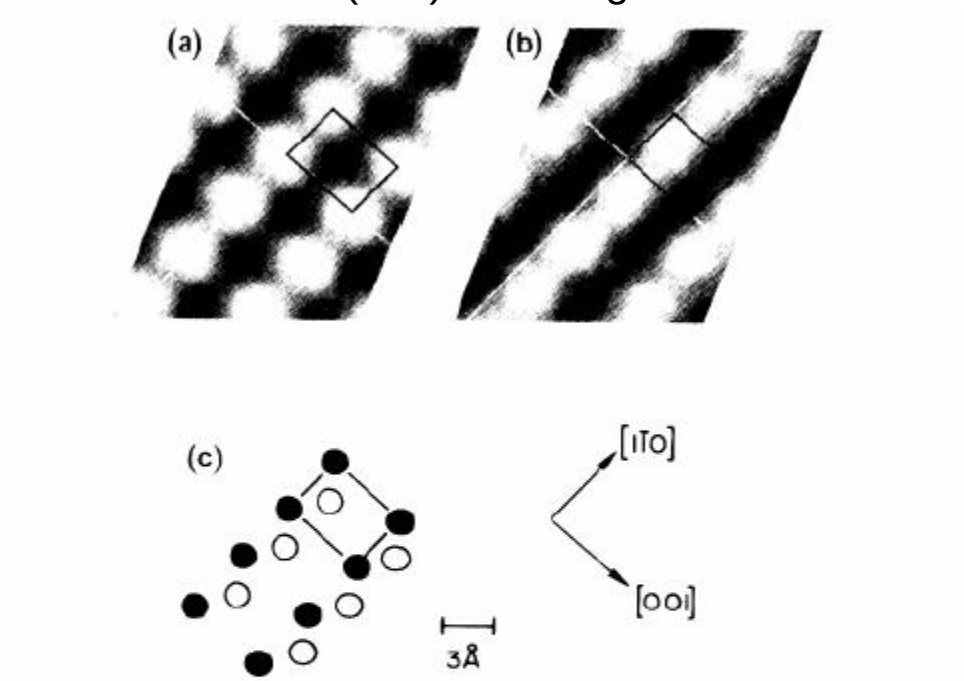
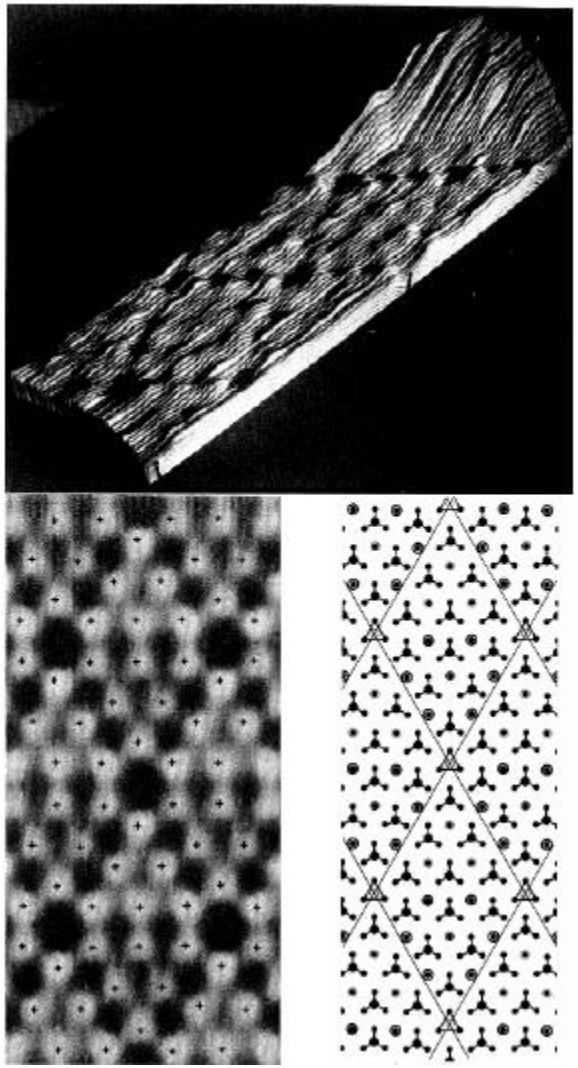


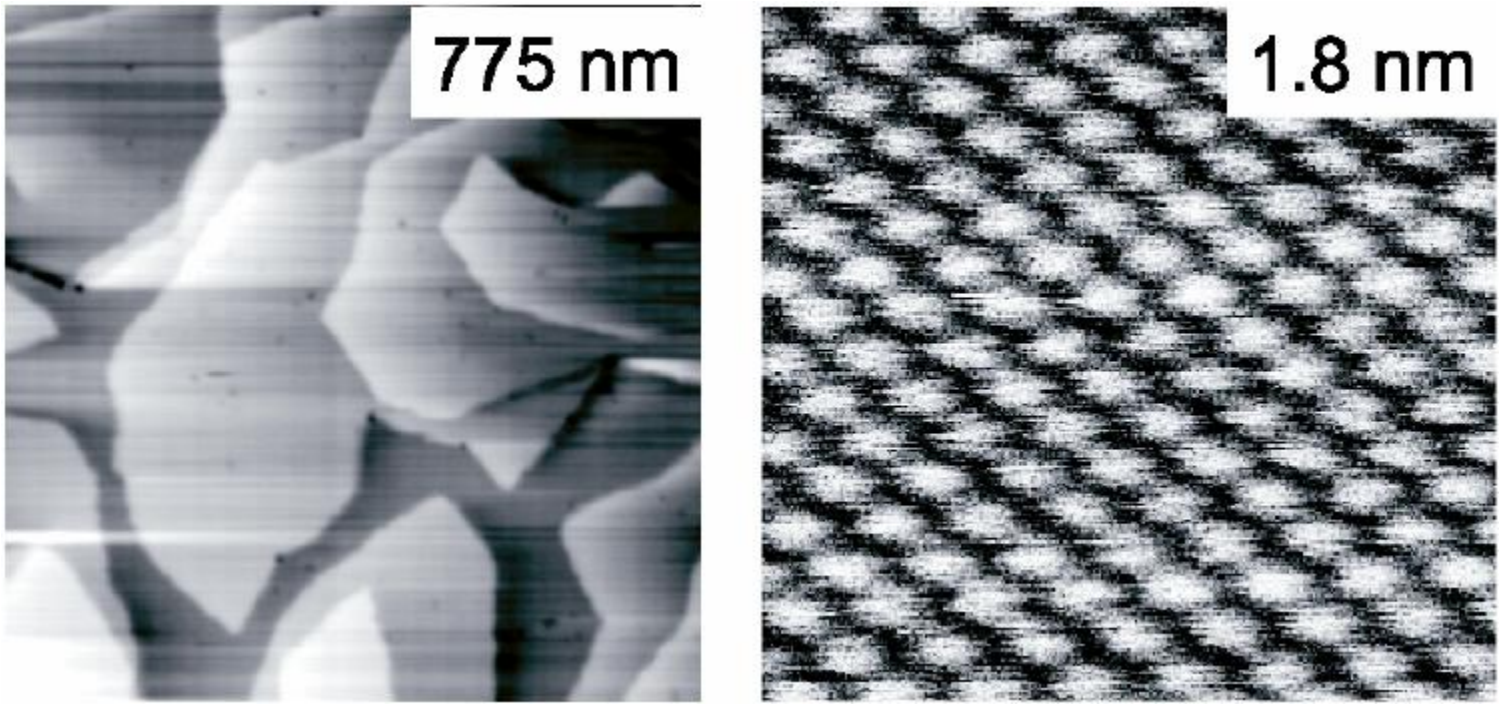
FIG. 2. Constant-current STM images acquired at sample voltages of (a) +1.9 and (b) −1.9 V. The surface height is given by a grey scale, ranging from 0 (black) to (a) 0.83 and (b) 0.65 Å (white). (c) Top view of the surface atoms. As atoms are represented by open circles and Ga atoms by closed circles. The rectangle indicates a unit cell, whose position is the same in all three figures.

Si(111) 7x7 image



- *Metals*

- first resolved by Binnig and Rohrer 1982 (Au(110)2x1 and Au(110)3x1 reconstructions)
- atomic resolution on a close-packed Au(111) by Hallmark et al. in 1987
- today, a large number of clean metal surfaces could be resolved, such as Cu(111), Cu(110), Cu(001), Pt(111), Pt(001), Ru(0001), Ni(001) and Ni(110)
- spacing between the atoms of the close-packed surfaces is 2-3 Å.
- corrugation heights are found to be rather large of the order of tenths of Å
- corrugation in contradiction with results from He scattering
- contradiction explained by force induced variation of tip-sample distance

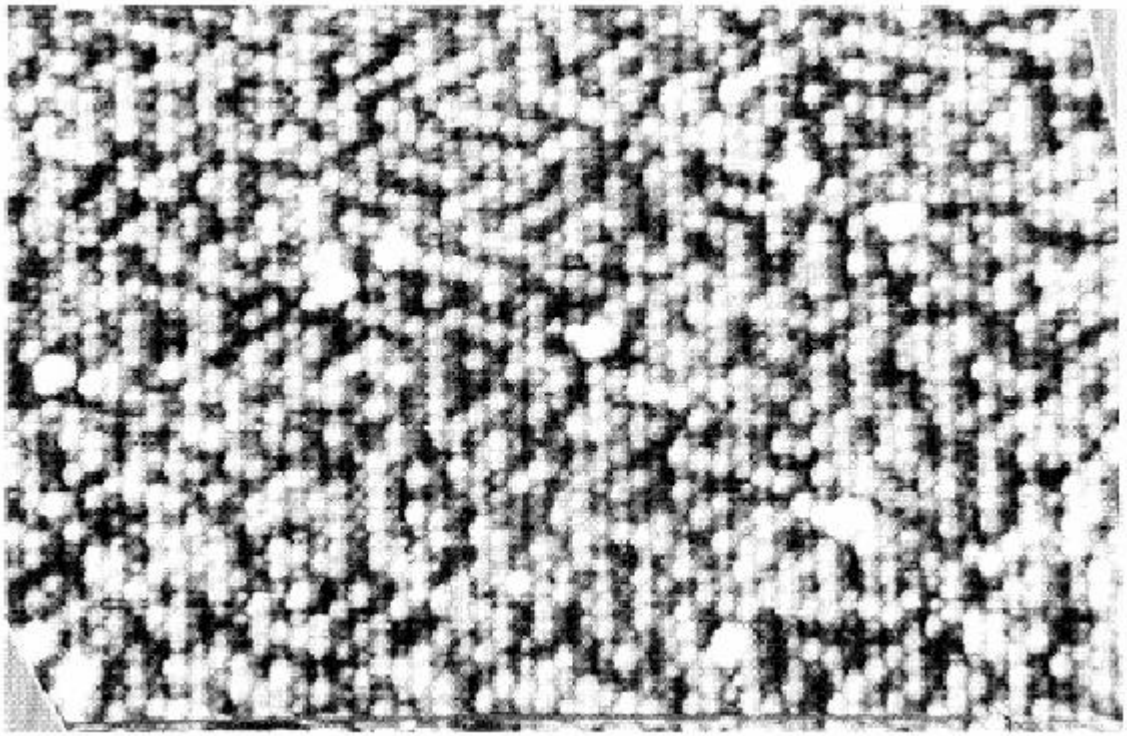


STM images of the Cu(111) surface in constant current mode. (left) Overview image with monatomic steps (right) Atomic resolution on Cu(111). The spacing between the protrusions is 2.5A.

- Superresolution on Metals

An impressive example of the resolution capabilities is given by Schmid et al., where Pt-atoms and Ni-atoms could be distinguished on a $Pt_{25}Ni_{75}$(111)-surface. The best resolution was observed with small tunnel resistances of (50-300 kΩ), which was attributed to the interaction between adsorbates at the tunneling tip and the surface atoms.

D. Eigler (IBM) calls these adsorbates “Behm amplifiers”. He often uses a Xe-atom that is picked up by the tip. Such adsorbates are only weakly bound to the tip. The strong force field between the tip and the sample leads to a modulation of the position of the adsorbate within the tip-sample gap. This causes an enhancement of the corrugation and superresolution.



- *Layered Materials*

- A number of layered materials, such as graphite or MoS2, could be resolved
- Especially, graphite has attracted a lot of attention, because of the giant corrugation heights.
- transition metal dichalcogenides, such as 1T-TaS2 or 1T-TaSe2, with atomic structure and charge density waves (CDW).
- Coleman et at published a review of the STM work of layered materials with CDW.
- Forces between tip and sample were attributed to play an important role.

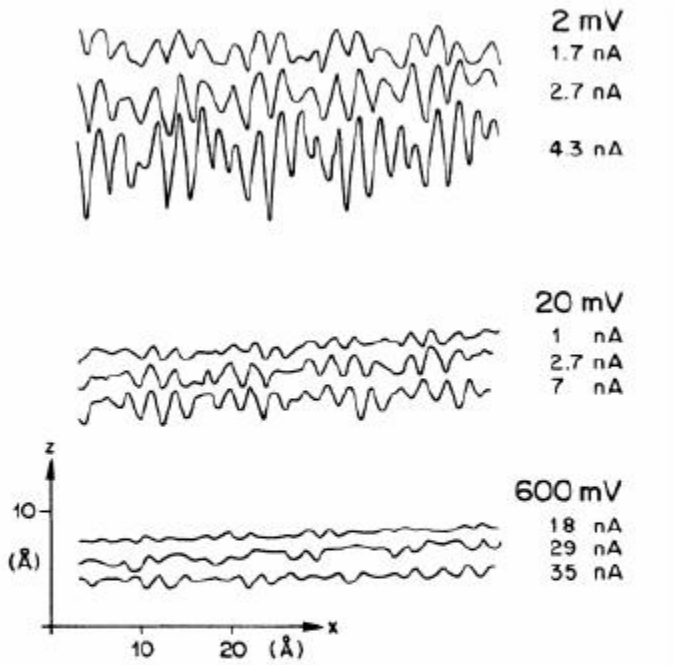


FIG. 1. Graphite STM traces obtained at ambient-air pressure and room temperature with a "pocket-size" STM (Ref. 14) with scanning speeds between 1 and 5 sec per scan. The varying corrugation within a scan is due to the mismatch between crystallographic and scanning directions (Ref. 3); plateaus in the traces indicate the saddle points in the LDOS (Refs. 3 and 11).

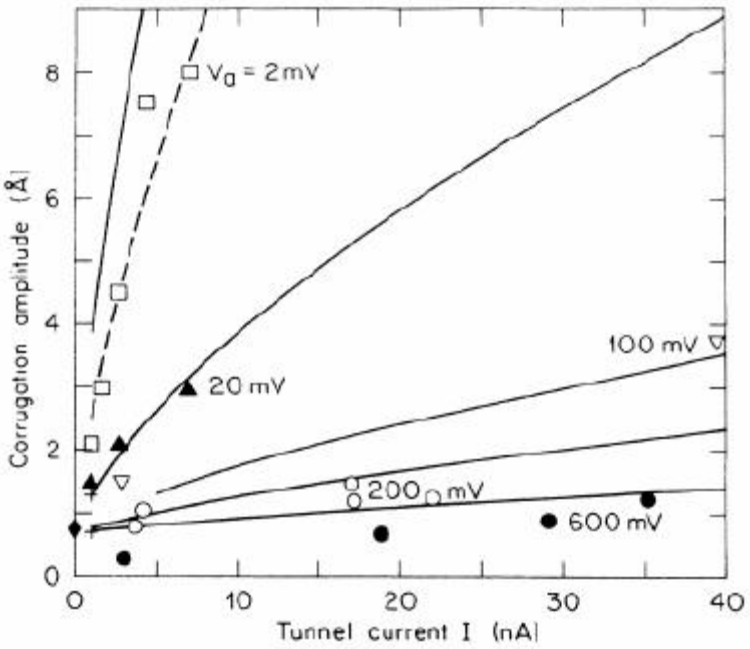
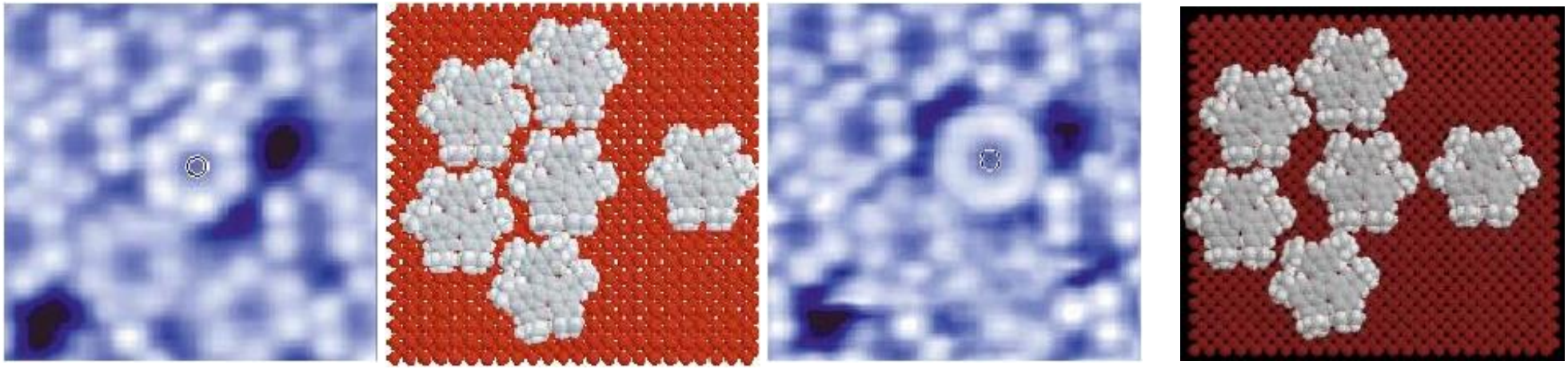


FIG. 4. Measured (symbols) and calculated (solid lines) corrugations as a function of tunneling current and voltage. The dashed line was obtained with $d^* = 0.4$ Å. The two crosses at 1 nA correspond to the measured corrugations at 50 and 400 mV, respectively, of Ref. 3; the diamond at zero current indicates the corrugation of the LDOS at the Fermi level (Ref. 11).

- *Molecules*

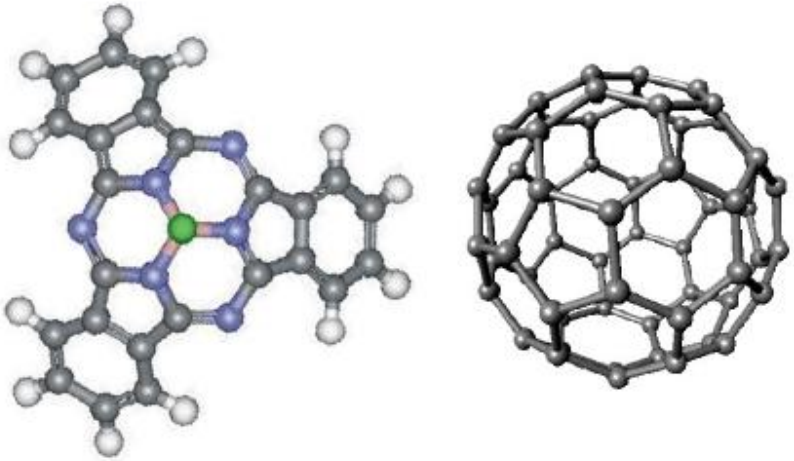
- First images of single molecules by Foster and Frommer.
- Liquid crystals and hydrocarbons 6 could be imaged.
- STM study of molecules in UHV.



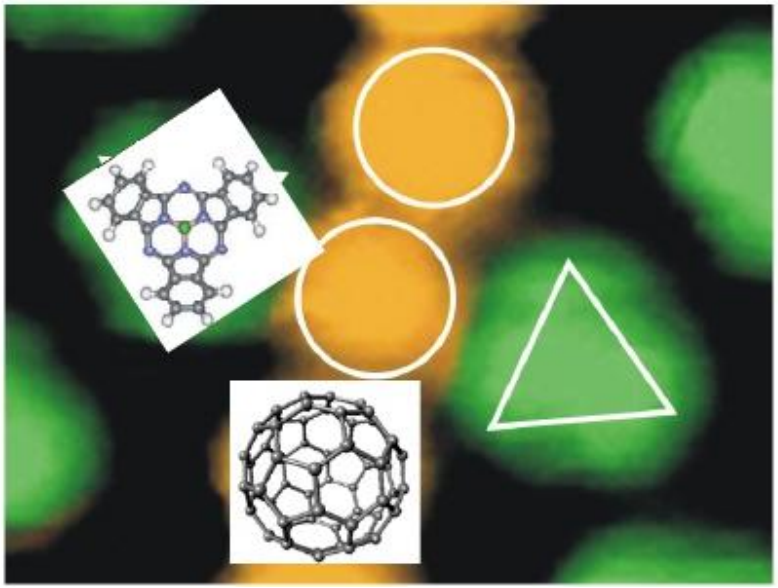
Two STM images on top show a six-lobed ”propeller” marked by an inner ring in an immobilized state close to four sister molecules (a) and in an rotating state when shifted away by one-fourth of a nanonometer (c) The graphical view of the computer simulation (b,d) illustrates the structure and the two positions of the molecular wheel.

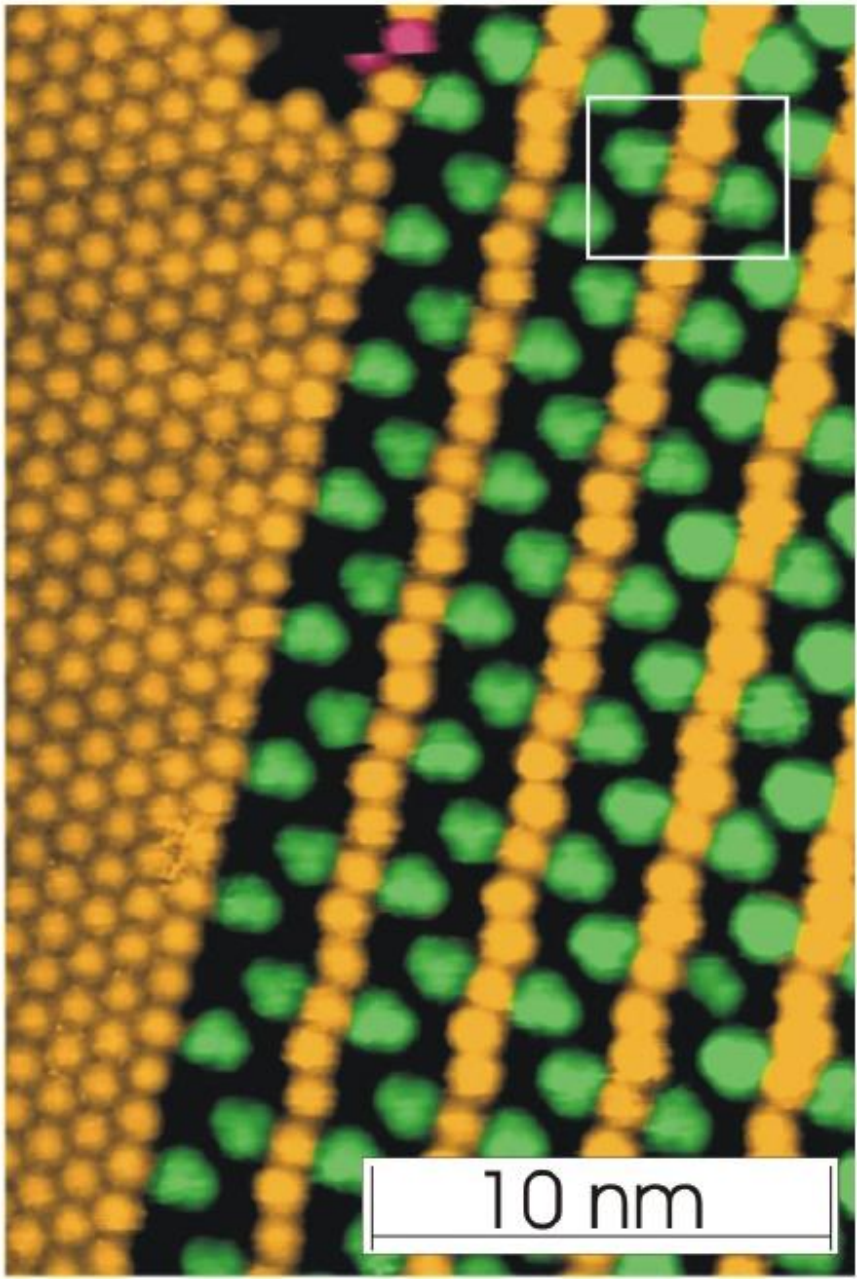
Generally, the mechanisms of tunneling through molecules are rather complicated, e.g., resonant tunneling may occur. Adatoms or small molecules (e.g., benzene molecules) which lie at on a surface can be imaged in most cases. Larger molecules can be more difficult to be imaged, because of poor conductivity. Especially, molecules which are oriented perpendicular to the surface may cause problems. E.g., alkylthiols on Au(111) can be best imaged with small currents of some pA. Larger currents lead to strong distortions of the image.

Chloro-[subphthalocyaninato]boron(III) on Ag(111)

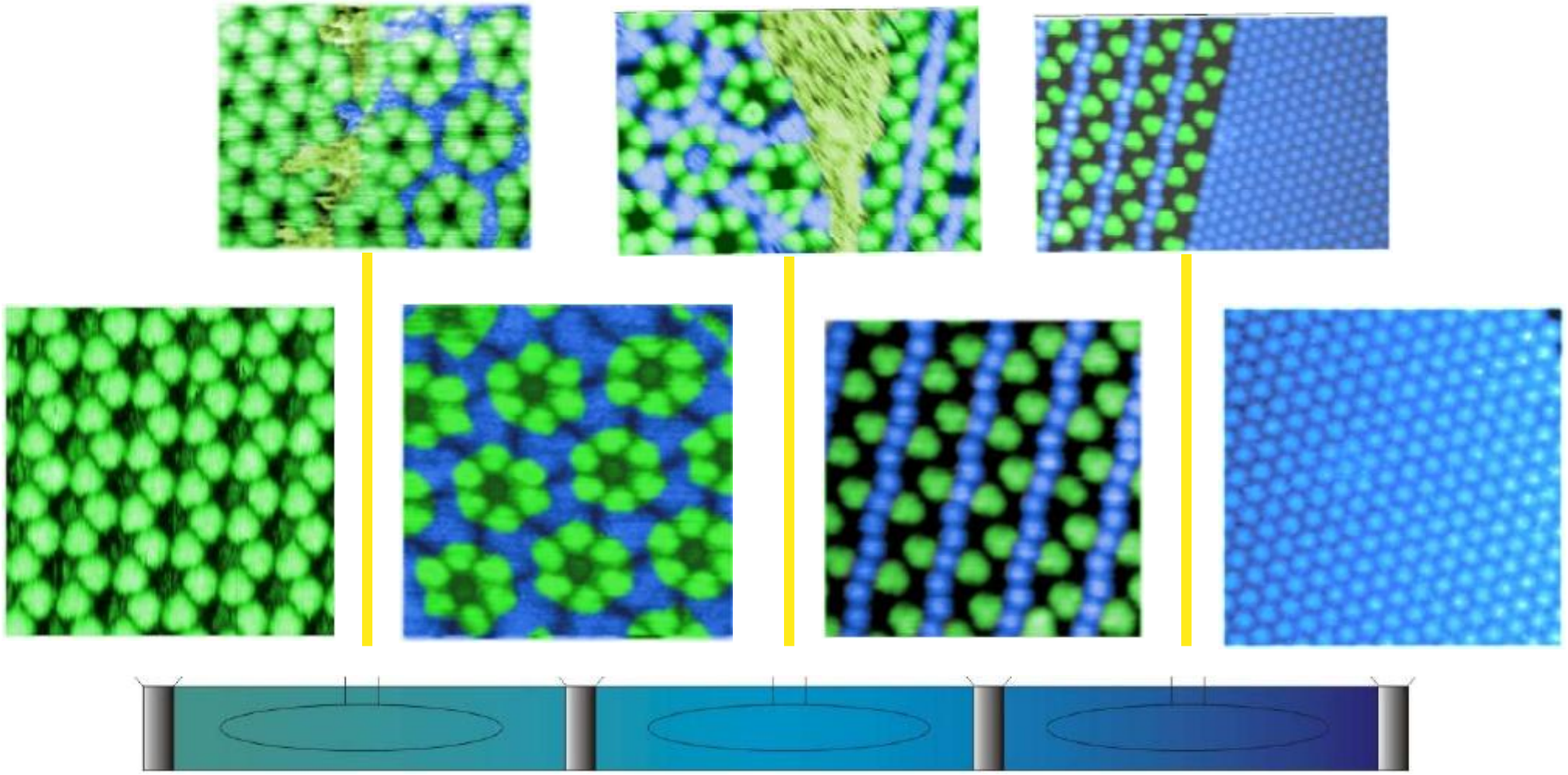


Chloro-[subphthalocyaninato]boron(III) & A C_{60}





Binary Phase Diagram of SubPC/C60



Scanning Tunneling Spectroscopy (STS)

- Spectroscopic Modes

Scanning tunneling spectroscopy (STS) experiments are important to determine properties, such as

- LDOS
- barrier heights

$$log(I) = -A\sqrt{\Phi}z + const.$$

There exist a variety of spectroscopic modes, variation of one externally adjustable parameter and measurement of tunneling current:

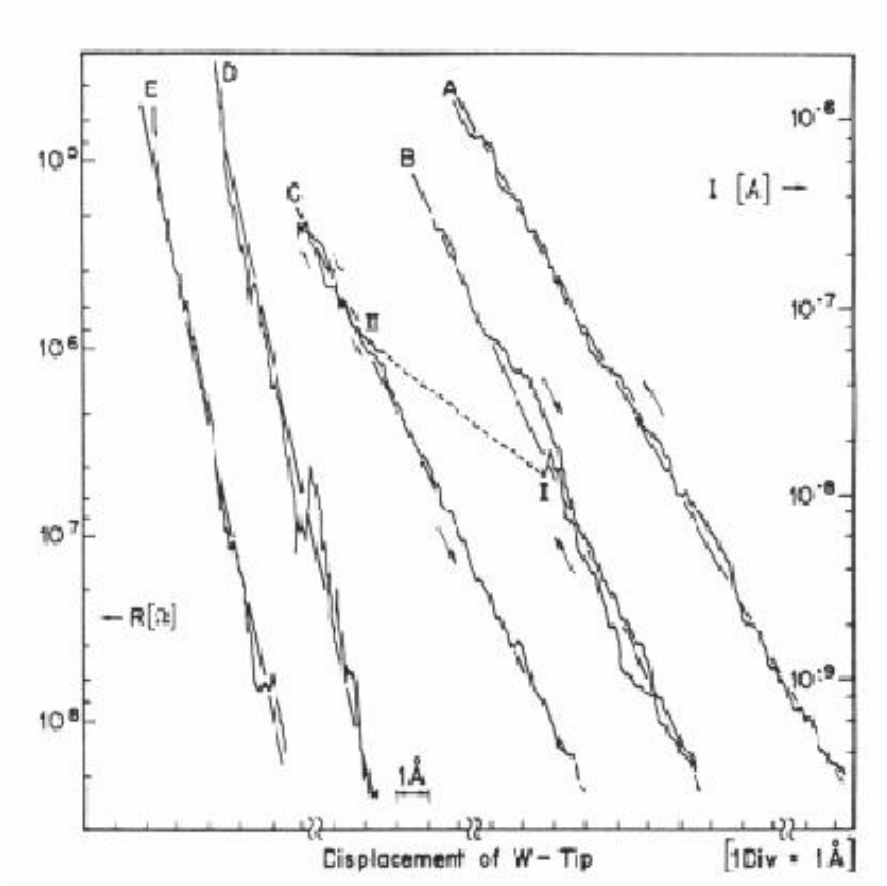
- voltage I(V) or dI/dV (often measured with lock-in amplifier)
- z-distance I(z), dI/dz (often measured with lock-in amplifier)

These curves can be either measured at a fixed lateral position or at various lateral positions (x_i,y_i). A simple way to get spectroscopic information is to acquire several images at different voltages or distances. Because of thermal drift this way is not ideal, but feasible. Alternatively, the tip can be stopped at different positions (x_i,y_i), the voltage or distance is ramped, and then the tip moves to the next position. In an ideal STS-experiment the tip DOS should be neglectable, which seems to be not always the case.

- *Barrier Height Measurements*

Barrier height: measure I as a function of z

$$log(I) = -A\sqrt{\Phi}z + const.$$

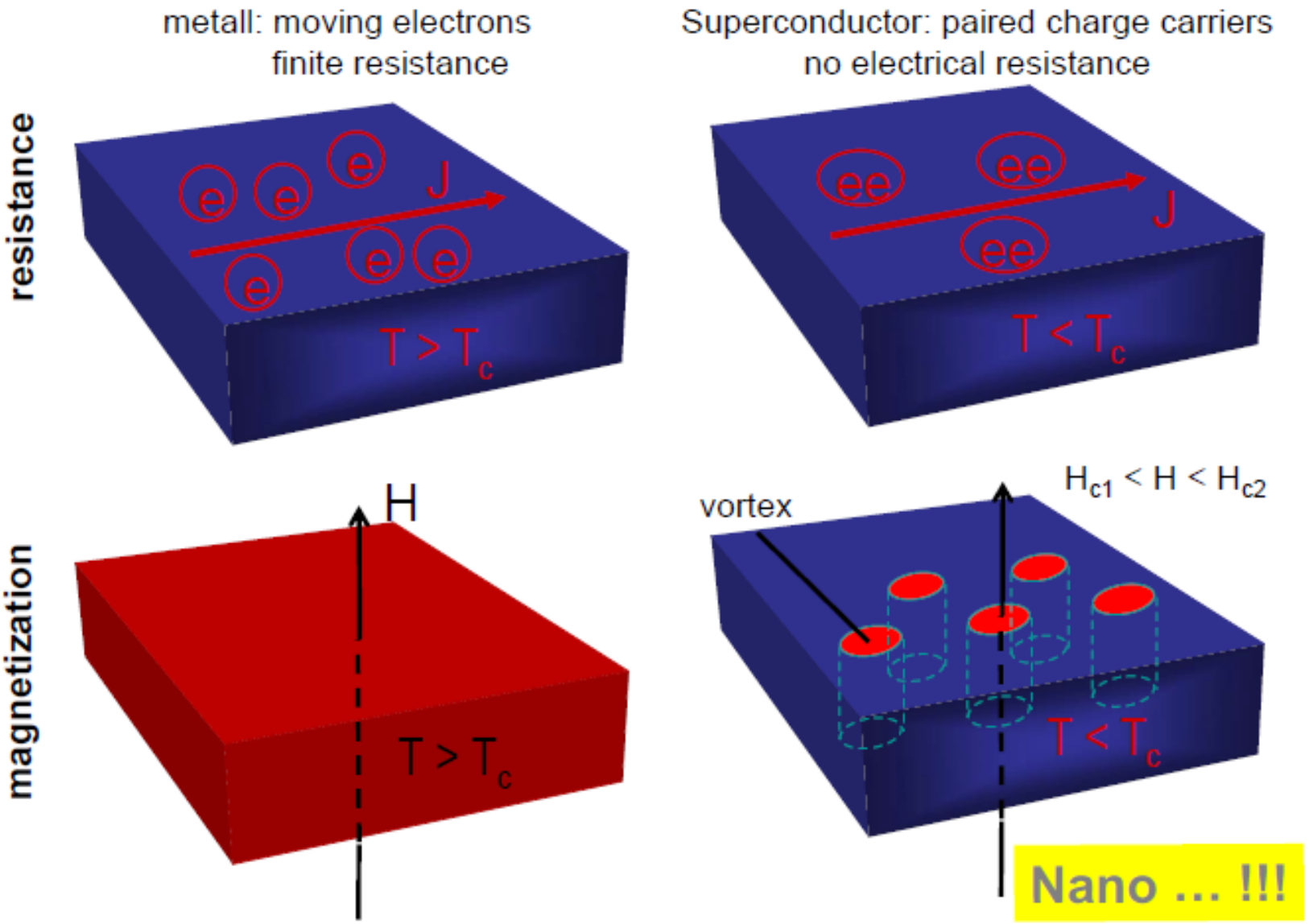


At the beginning of the experiment, barrier heights of 0.6-0.7 eV were found. By successive in situ cleaning procedures barrier heights of up to 3.5 eV were found, which is close to the expected value of 4-5 eV. The small values at the beginning of the experiment were related to contamination of the tungsten tip, e.g., oxide layers or hydrocarbons/ water layers. The curves represent the first observation of vacuum tunneling through a controllable gap.

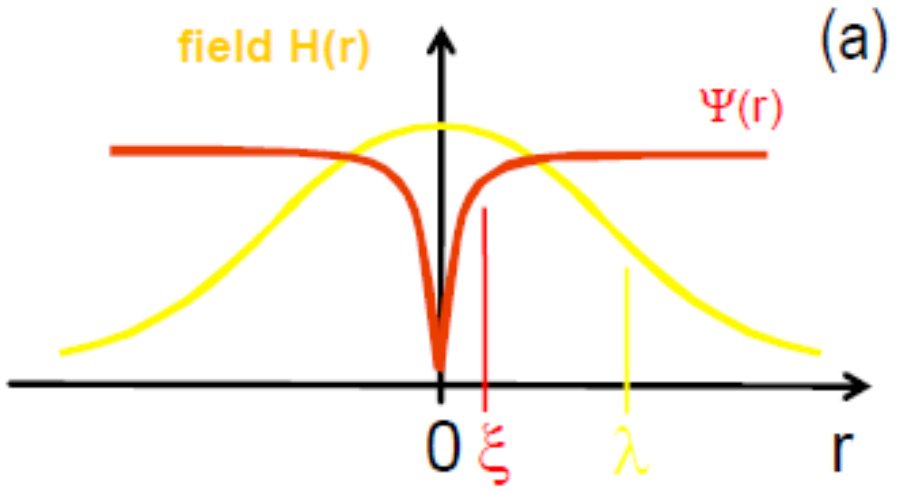
However, the barrier heights found in STM experiments are often smaller than expected. This is explained by an elastic deformation of the tip (and/or the sample) cause by attractive long- and short range forces. The tip-sample distance is decreased below the experimentally set value by the acting attractive forces.

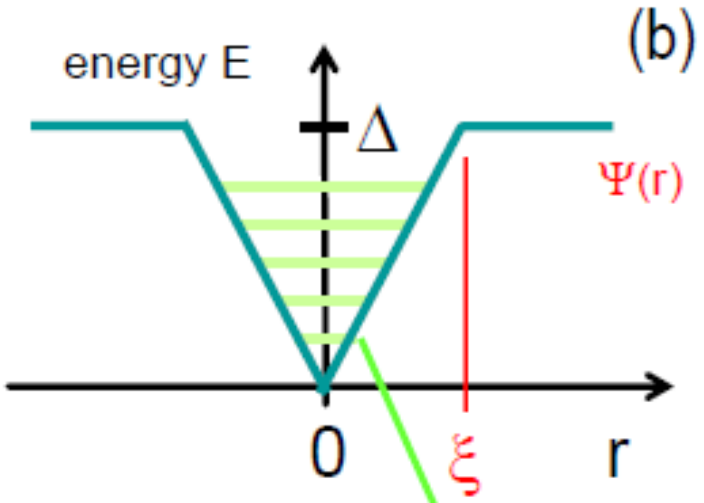
STS on Superconductors

- Basics of Superconductors

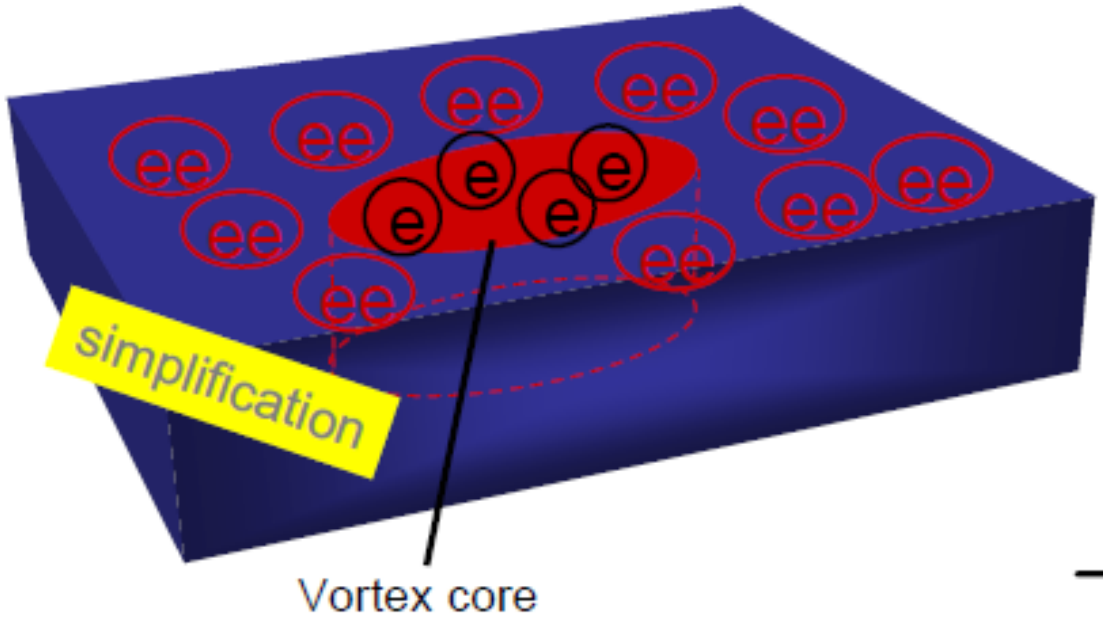


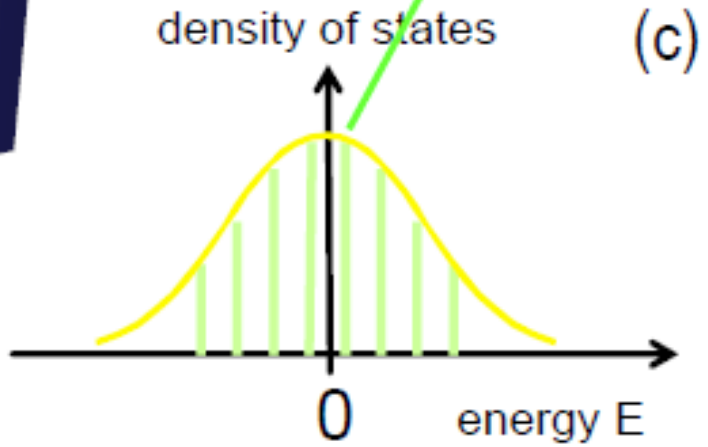
- *Vortices*





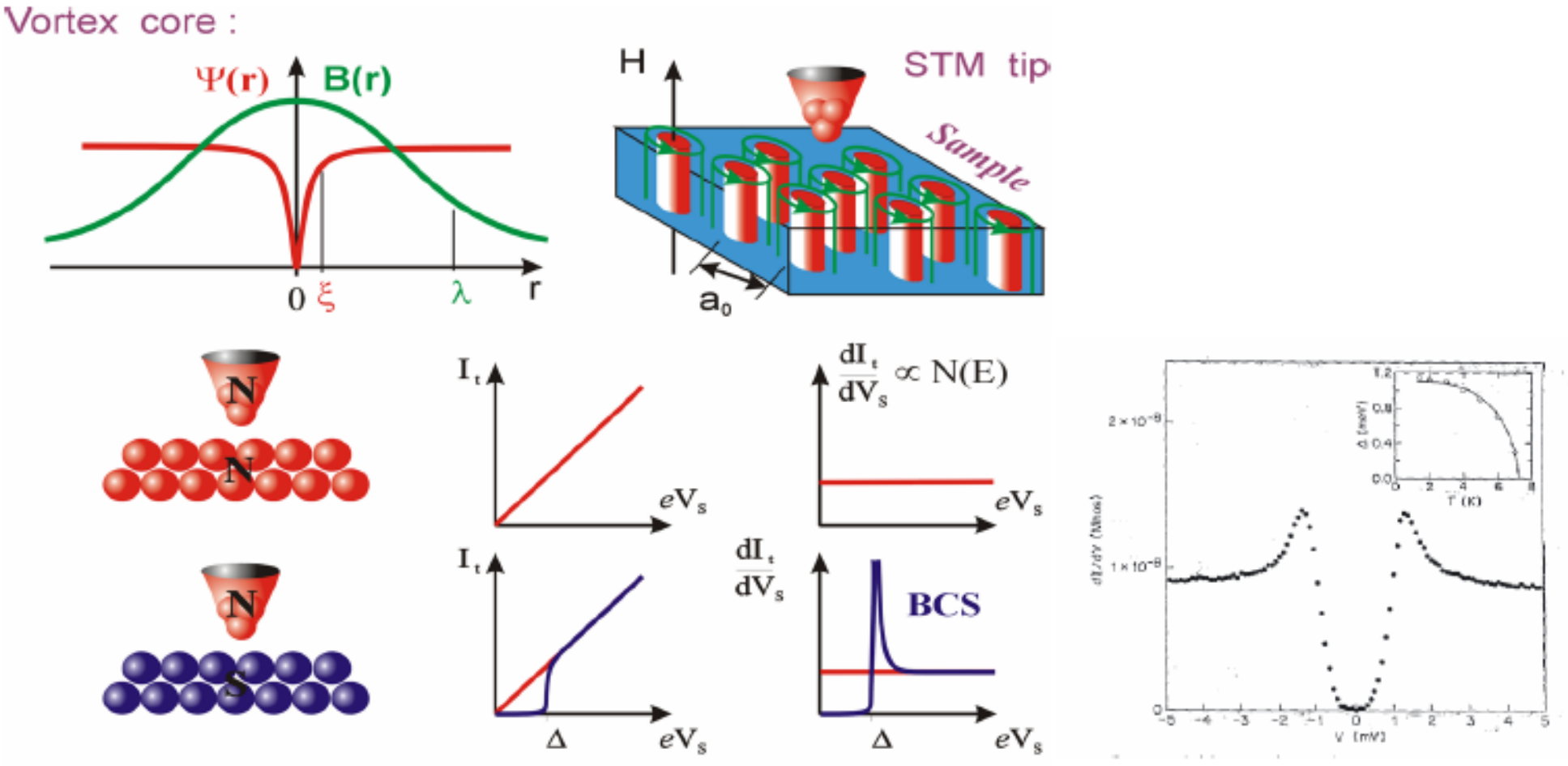
localized states





The STM is sensitive for electronic states !

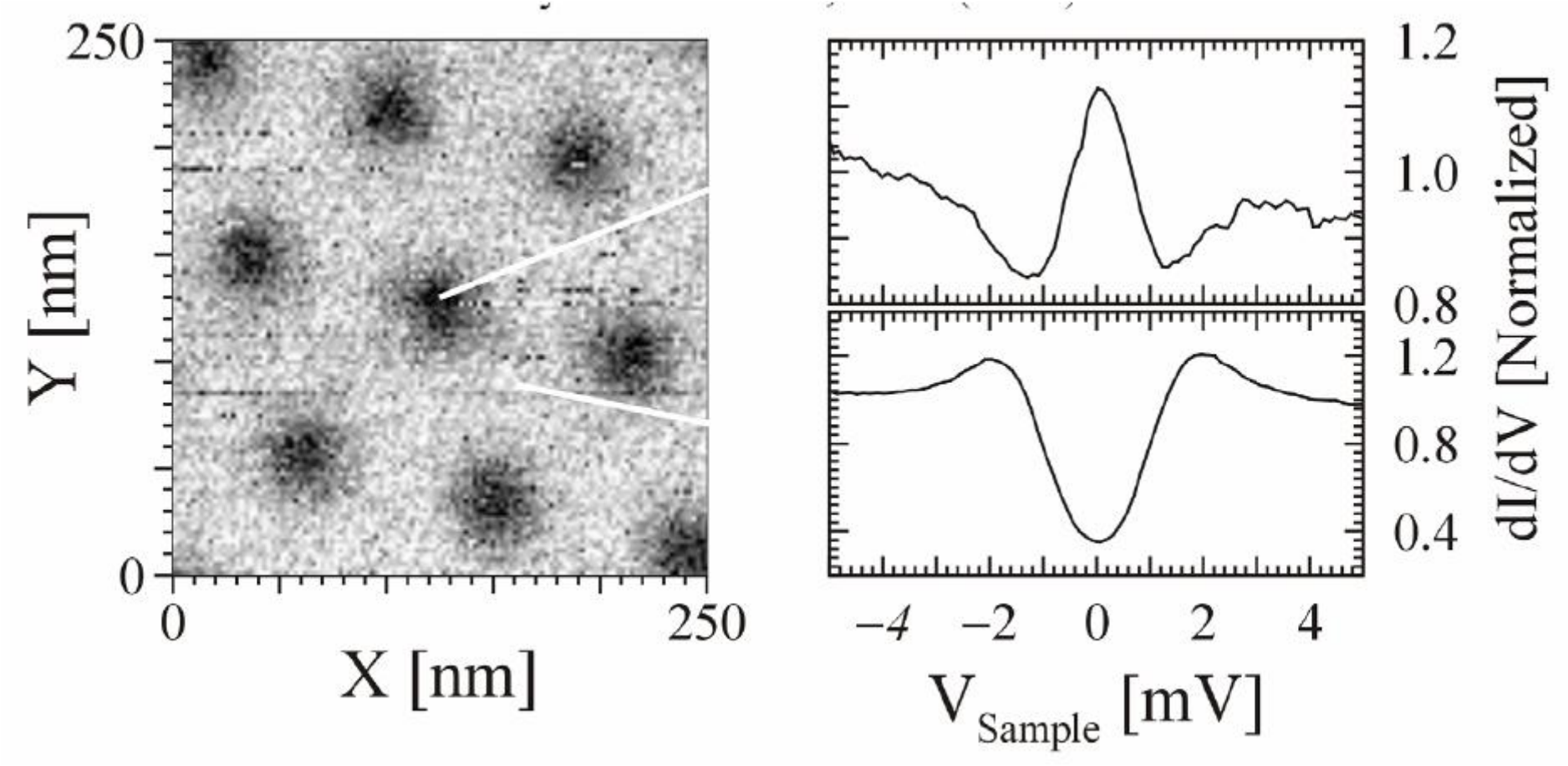
- *Principle of Vortex Imaging*



the imaging of vortices is based on the difference between the spectra of the vortex core and the spectra outside the vortex, i.e. in the superconductor.

- Electronic States of a Vortex

2H-NbSe2 1.3 Kelvin, 0.3 Teslas

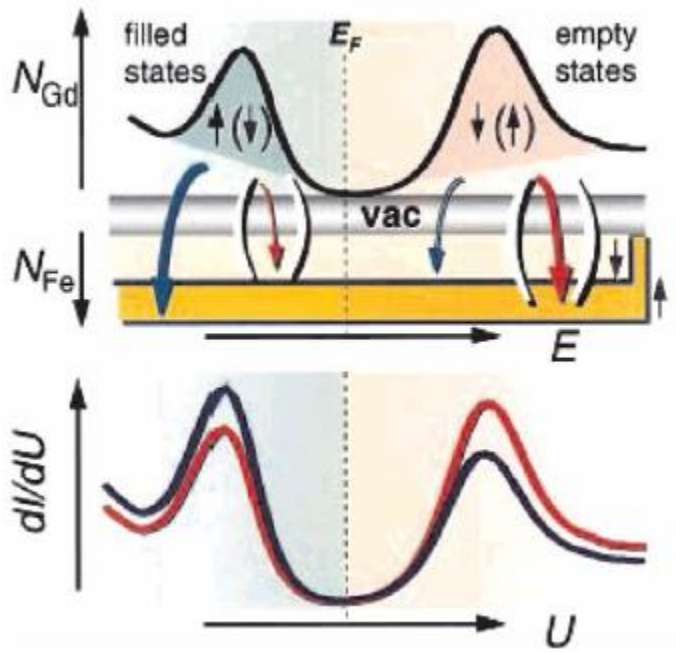


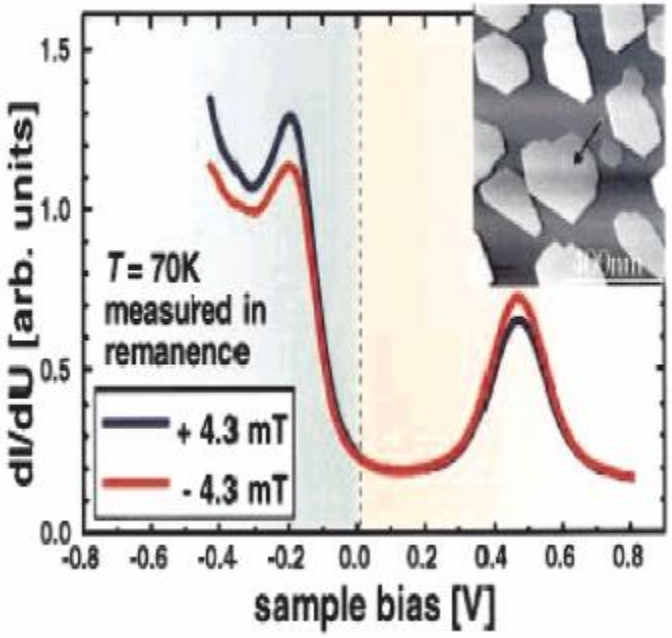
Spin Polarized Tunneling

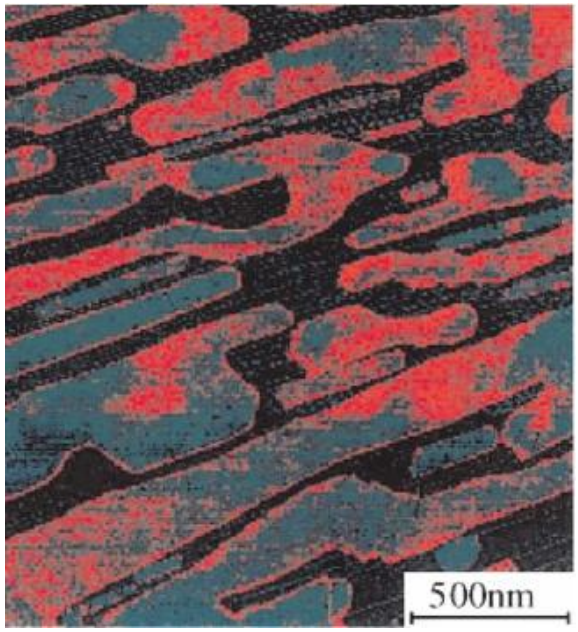
Recent developments in spin-polarized scanning tunneling microscopy and spectroscopy have led to an unprecedented insight into magnetism at the nanometer length scale and, in some cases, even down to the atomic level. The correlation between structural, local electronic and local magnetic structure can now be studied beyond the exchange length.
Select tip magnetization by:

- Fe-coated W tips: in plane (perpendicular to tip axis) –> in-plane component
- FeGd coated W tips: perpendicular (along tip axis) –> perpendicular component
- for samples with low coercivity use antiferromagnetic coatings (Cr)

Principle (on Gd(001) imaged with Fe coated W tip):

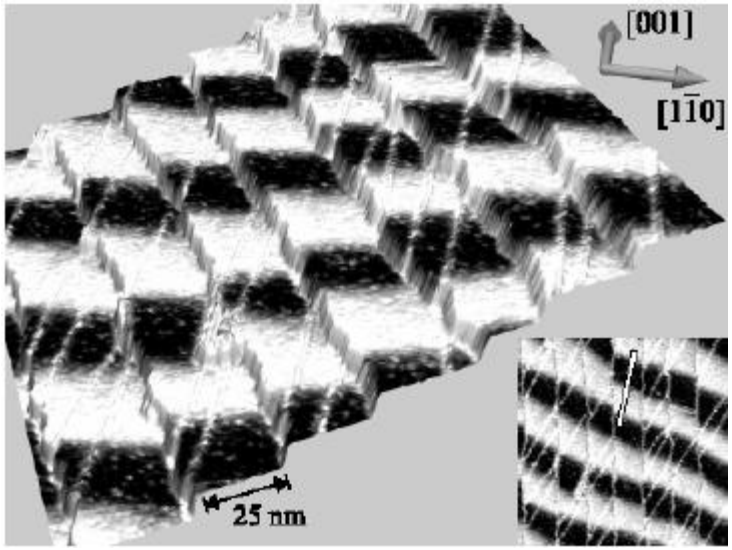




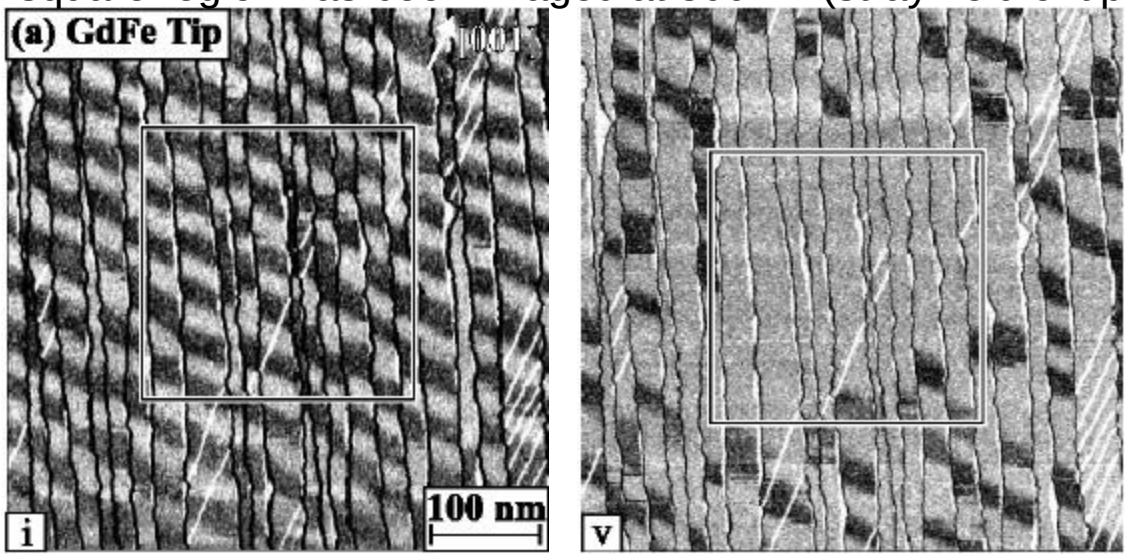


- *Magnetization Components of 2ML-Fe on W(110)*

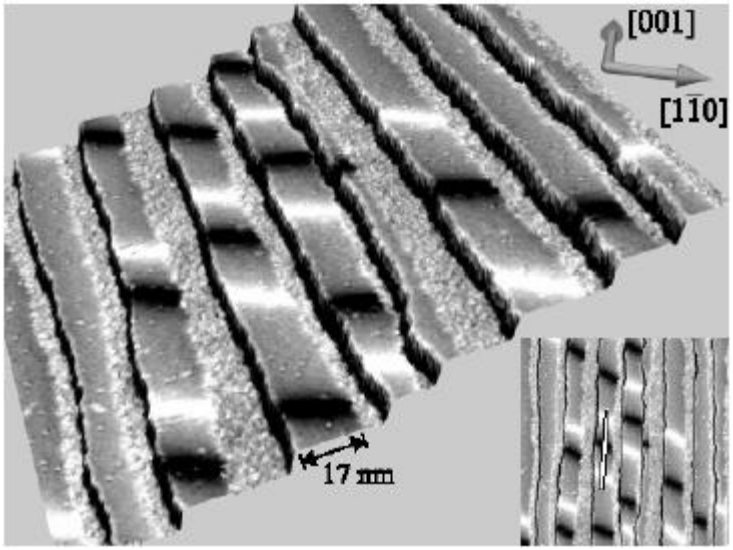
Fe-coated W tip: in-plane component



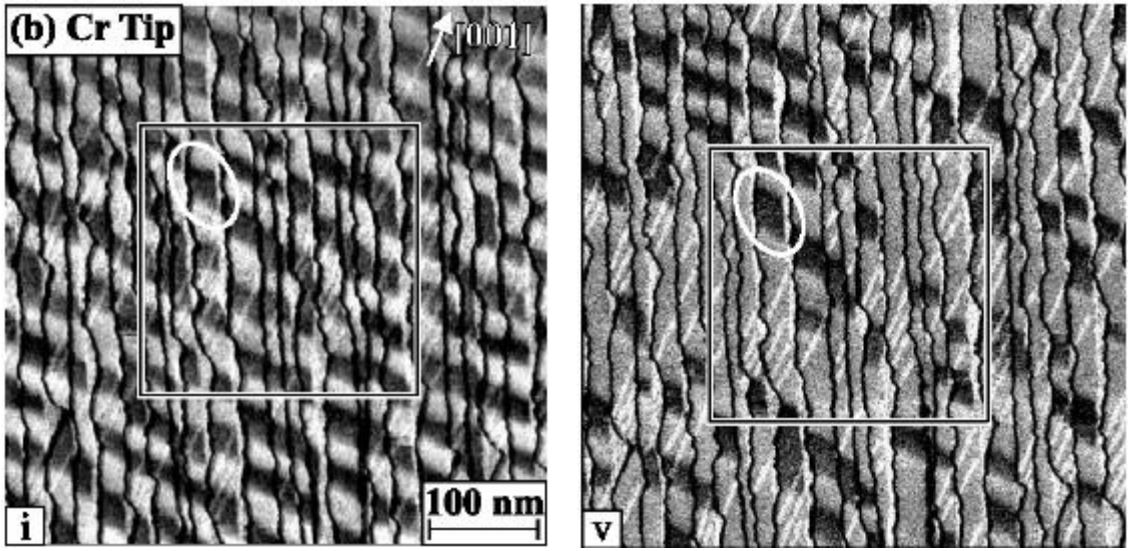
square region has been imaged at 800mT (stray field of tip!)



FeGd coated W tips: perp. component



square region has been imaged at 800mT (with Cr tip!)



In-plane and perp. Magnetization components can be imaged. Cr tips are stray field free.

- *Atomic Resolution of antiferromagnetic Mn on W(110)*

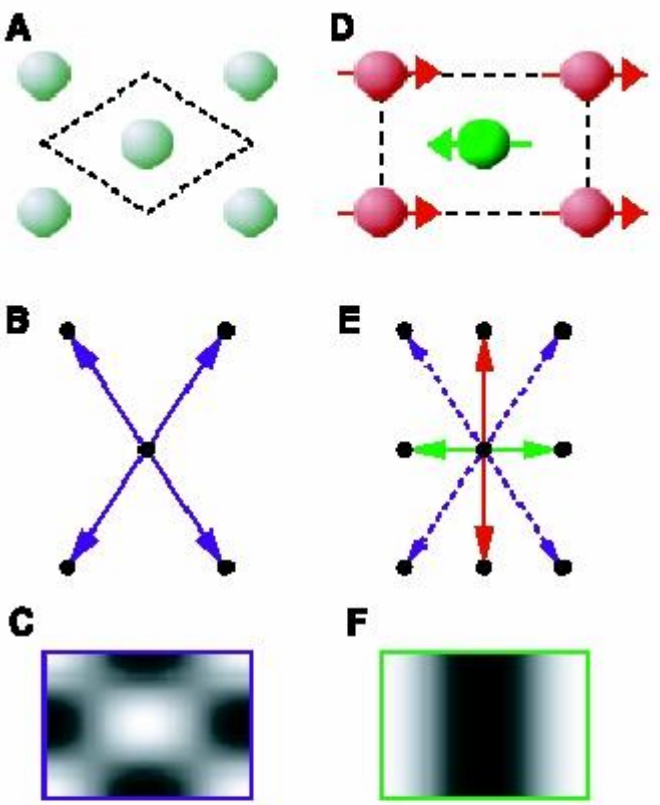
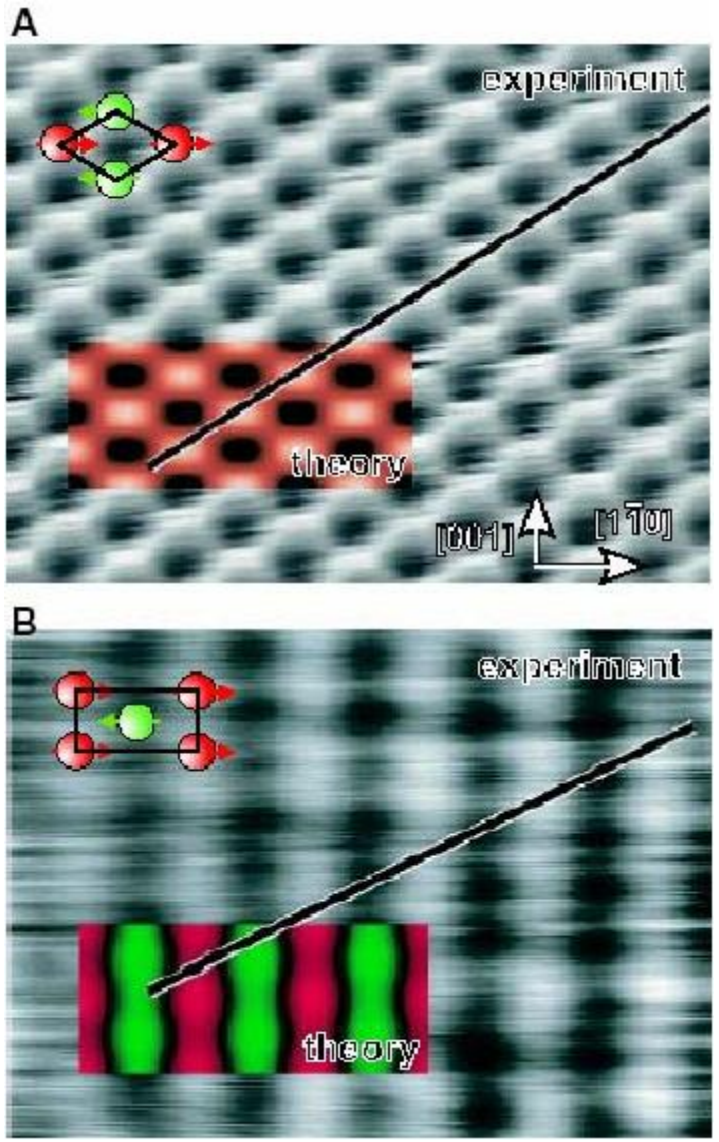


Fig. 3. Lattice (**A** and **D**), shortest reciprocal lattice vectors (**B** and **E**), and the expected STM images (**C** and **F**), associated to the shortest reciprocal lattice vectors of the chemical (left) and the magnetic (right) unit cell of a Mn ML on W(110). Note that (E) contains the shortest vectors of the chemical unit cell (dashed lines) and the two inequivalent pairs of additional vectors due to the magnetic superstructure.



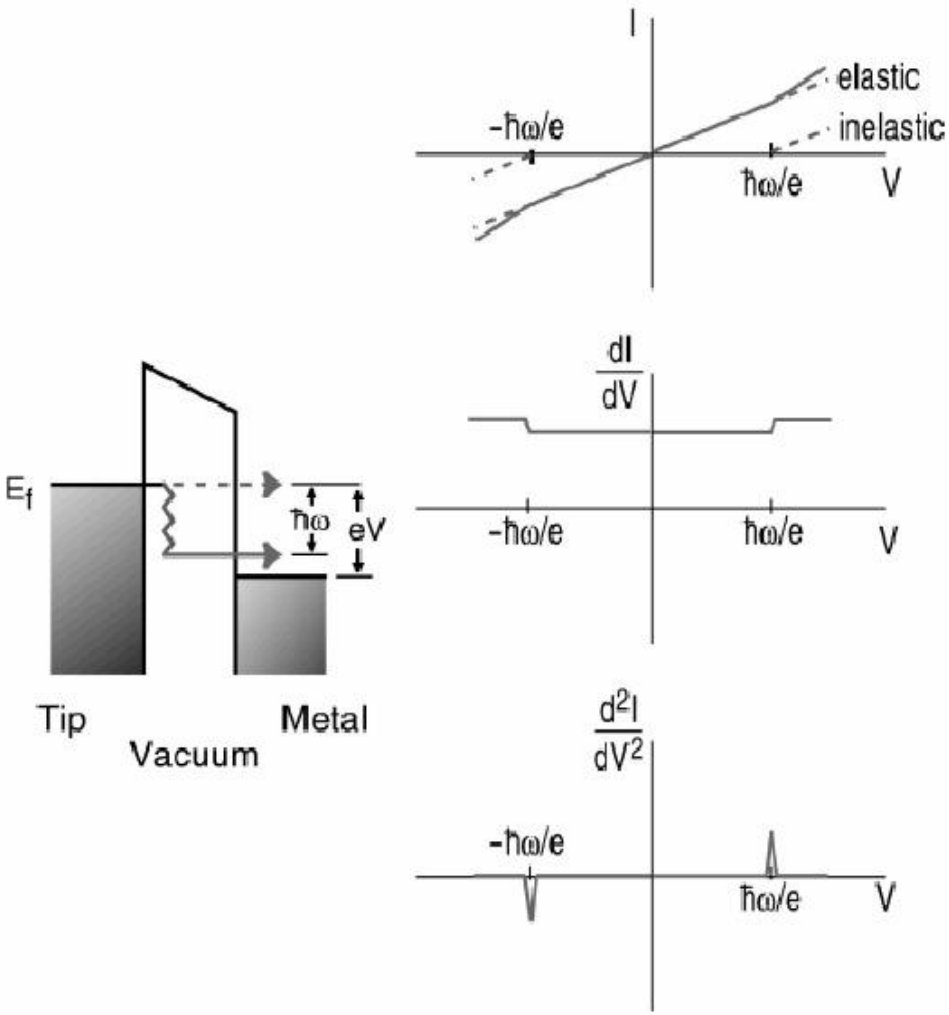
The larger lattice vector leads to a longer decay length of the electronic surface states. Therefore only these states are imaged with the magnetic tip. The observed periodicity has doubled.

Inelastic Tunneling Spectroscopy

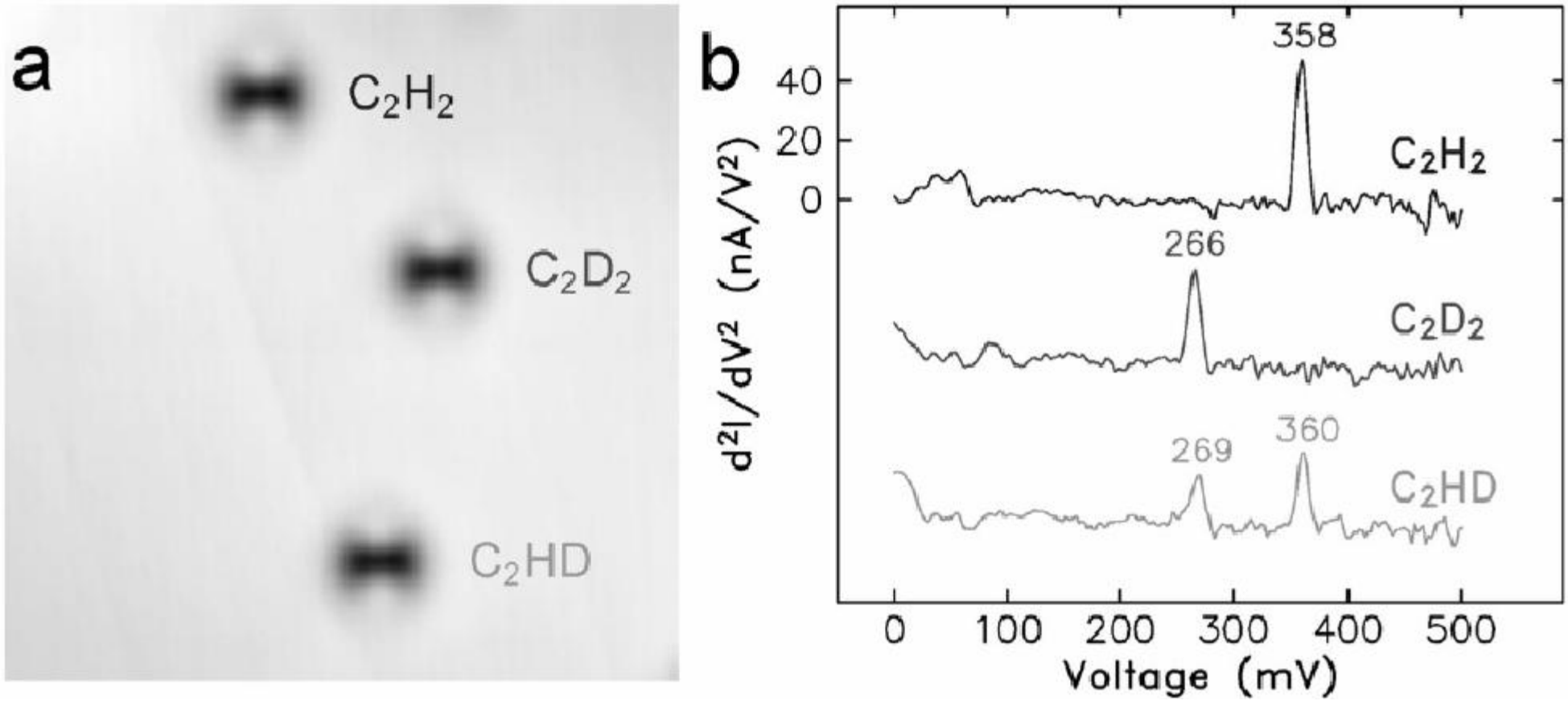
Schematic showing the emergence of inelastic tunneling at the threshold for vibrational excitation.

The change in the tunneling current due to vibrational excitation is too small to be measured from the *I* –*V* curve. While a change in the differential conductance, dI/dV, can be seen for strong modes, more often vibrational features needs to be extracted from d^2I/dV^2. An important characteristic of vibrational inelastic electron tunneling spectroscopy is the occurrence of a peak of the opposite sign on the negative bias side.

Lacking an isotope shift analysis, the assignment of a feature to vibrational excitation needs to be confirmed by a corresponding feature with the opposite polarity at the opposite bias. This schematic depicts an increase in the conductance, associated with a positive/negative peak for positive/negative sample bias. In contrast, electronic spectra arise from elastic tunneling peaks are positive and occur on either positive (unoccupied) states or negative (occupied) states !



Vibrations of Chemical Bonds



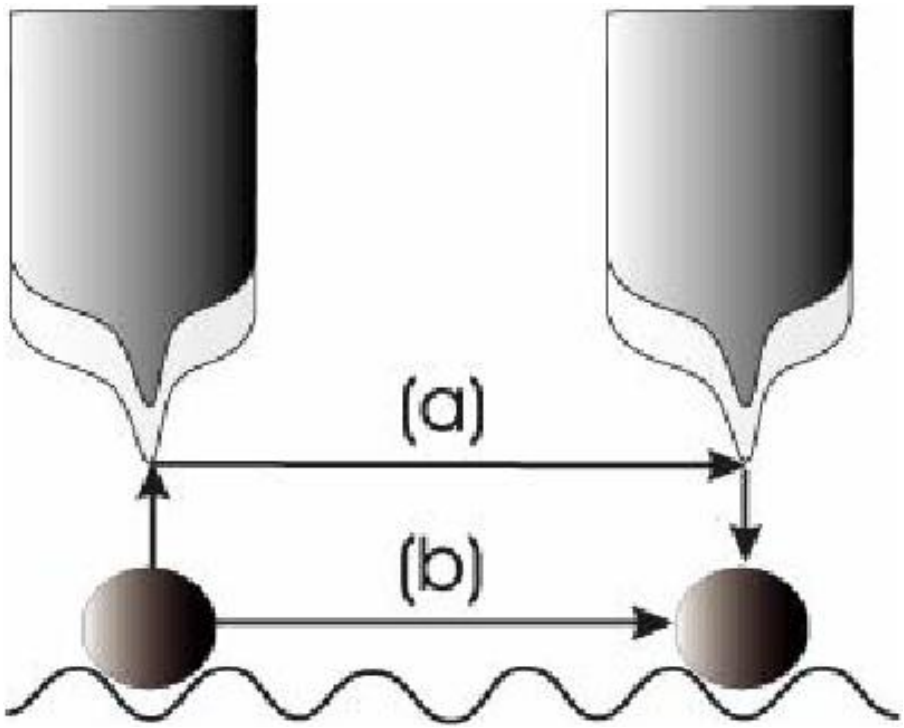
56 Å x 56 Å STM topographical images and single-molecule vibrational spectra via STM-IETS of three acetylene isotopes on Cu(001) at 8 K. The two protrusions bright in the image of each isotope are due to the presence of the C–H and C–D bonds while the central depression dark is attributed to the C–C bond. The C–H stretch is observed at 358 meV for C_2H_2 and the C–D stretch is observed at 266 meV for C_2D_2. Small upshifts are found for the C–H and C–D stretches of C_2HD. The C_2HD spectrum demonstrated for the first time single bond sensitivity with STM-IETS.

Manipulation by STM

- Manipulation of single Atoms

a) Vertical manipulation (transfer of the surface atom to the tip and back to the sample): The transfer of the adsorbate atom from the surface to the tip, or vice versa, is achieved by approaching the tip into contact or near-contact. The application of voltage pulses can be used to set the direction. Eigler found that Xe atoms moved in the same direction as the tunneling electrons, which was related to heating-assisted electromigration.

b) Lateral manipulation mode (adsorbate is kept adsorbed to the surface and moved laterally along surface): The tip is moved to the initial point, the set point is increased by about 2 orders of magnitude, which corresponds to a decrease of the distance of several Angstrom. The tip forms a weak bond with the adsorbate atom or molecule. The tip is then moved along the line of manipulation. Typical threshold resistances to slide an adsorbate are 5MOhm for sliding Xe along rows of Ni(110), 200 kΩ for sliding CO along Pt(111) and 20 kΩ to move Pt adatoms along Pt(111).

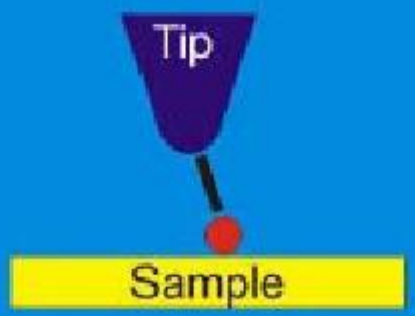


- STM Manipulation Mechanisms

Forces:

U=0, I=0

Pulling, Pushing
Sliding of Atoms



Electric Field:

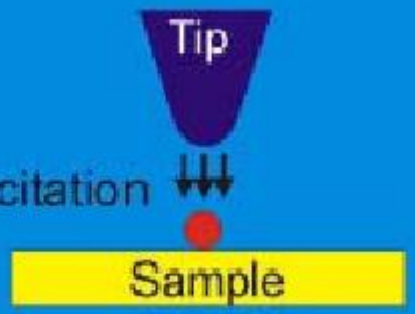
10^{7} - 10^{8} V/cm

Field evaporation
Field assisted diffusion
Stark effect

Electric Current:

10pA - 100nA

Inelastic tunneling
Electronic/vibrational excitation
Local heating



- STM Manipulation of single Fe-Atoms On a Cu(111) surface