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Materials & Surfaces

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Why are surfaces important ?

- **Determine adhesion and friction between solids (ice skating)**
- **Determine how a liquid wets a surface (Babylonians, Pliny, Franklin)**
- **Allow the production of chemicals through catalysis**
- **Give rise to interesting electronic properties**
- **Determine the optical appearance**

Surfaces covered just by ONE LAYER OF MOLECULES

One layer is enough to completely alter the surface :

Ice is slippery above 230 K but not below.

This is why Robert Falcon Scott died of exhaustion during his South Pole expedition

But we do not want to leave to nature what the surface does, we want to determine what it does...

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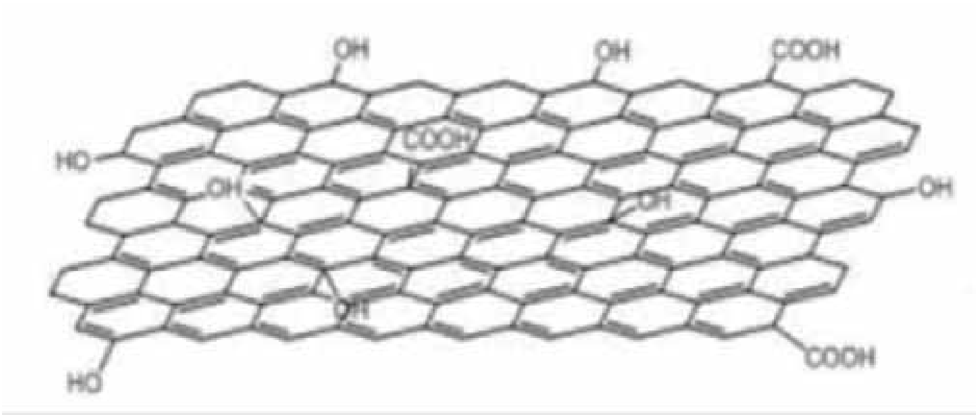
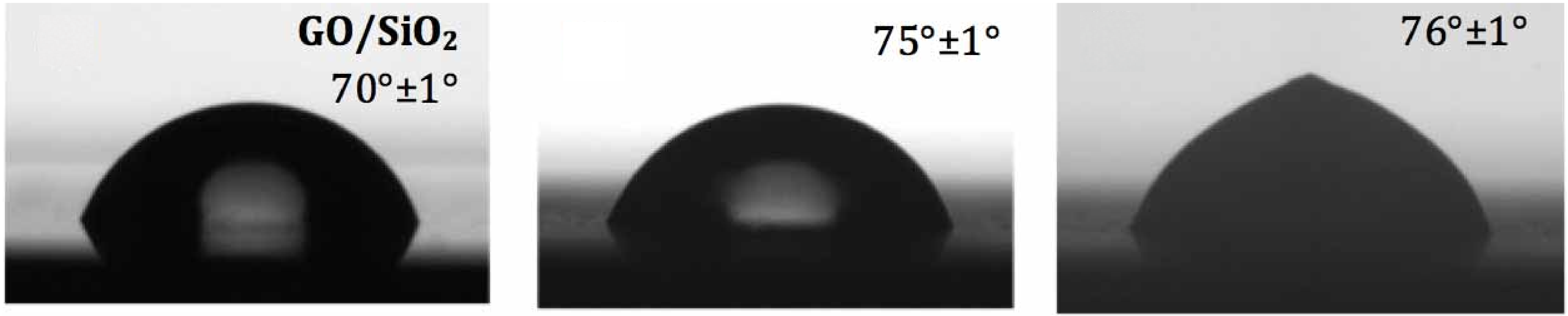
Of course you can change the icing properties with one single layer of atoms…

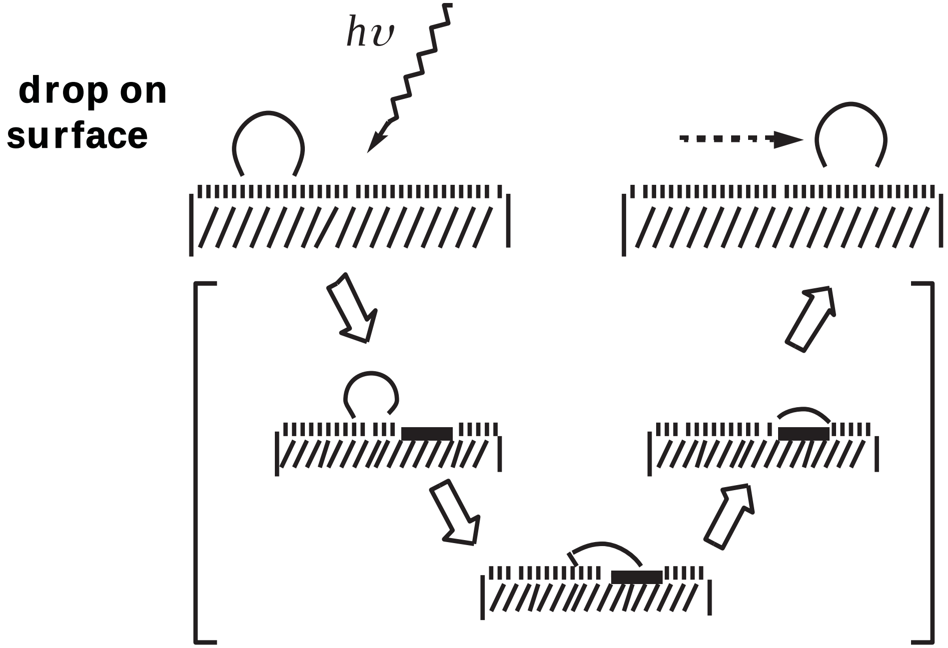




Graphene oxide delays freezing onset by 10ºC

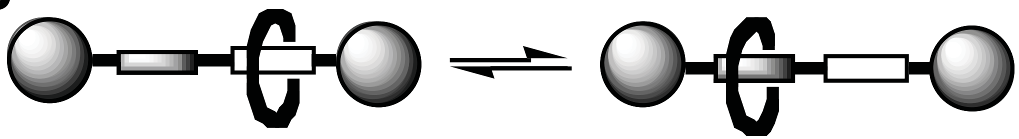
Surface with functional molecules

We want to graft molecular motors on a surface and make them move in such a way that a drop of liquid wants to go to the part of the surface where the molecules have moved



What molecule have the synthetic chemists prepared for us?

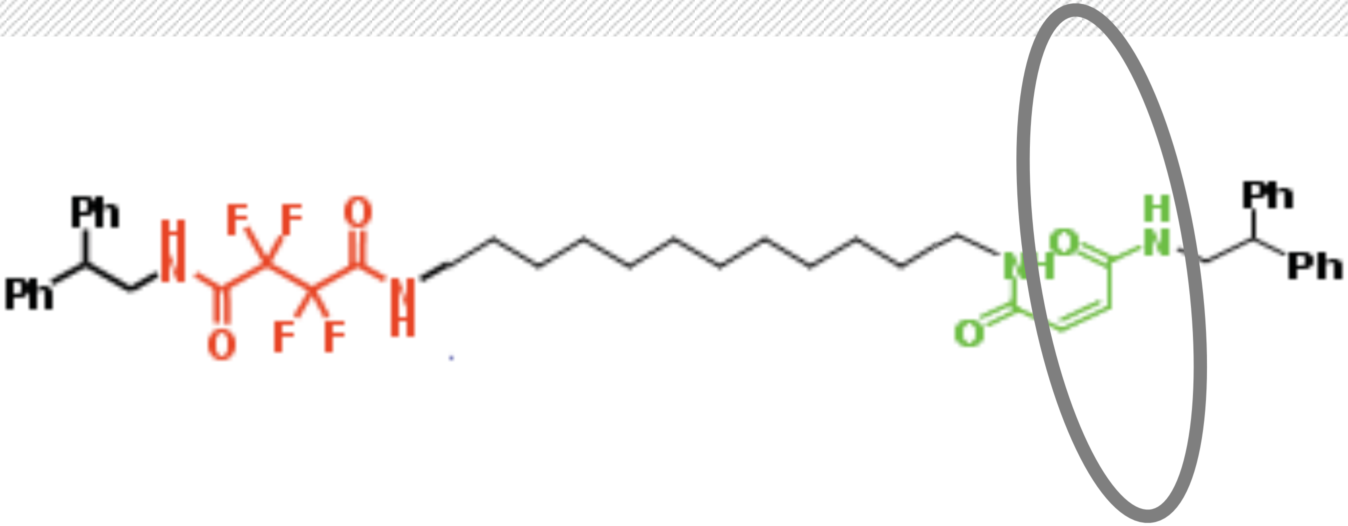
- **We need a rotaxane that moves when stimulated by light**



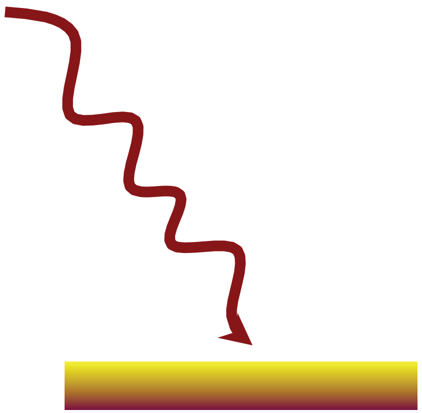
Linear motion in a rotaxane (a "molecular shuttle")

- **We need a surface on which a drop wets when the macrocycle is in one position and does not wet when it is in the other position**

Remember how a teflon pan behaves compared to other surfaces you know

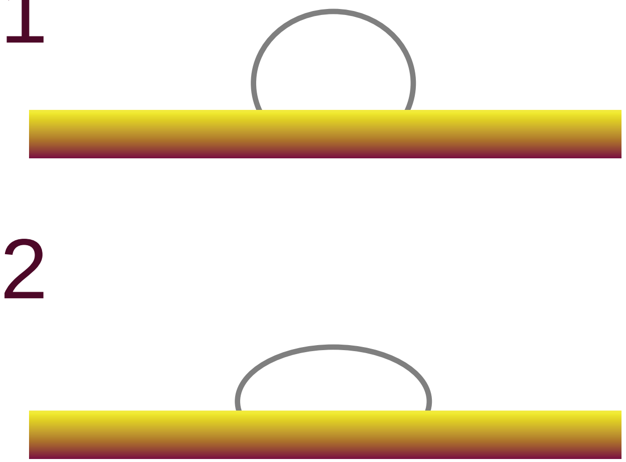


UV- light (240-400nm)

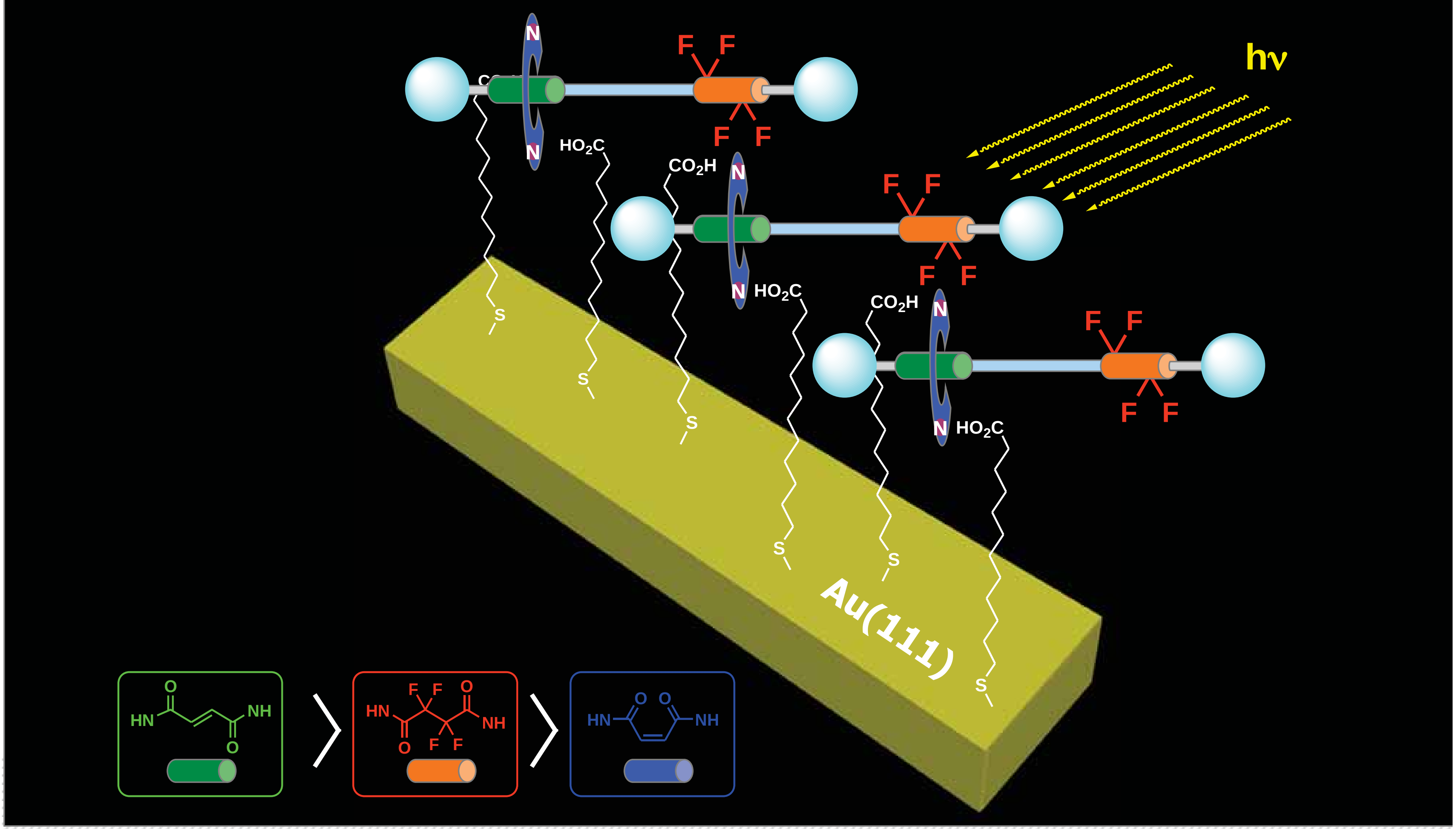


1

2



Hydrophilic

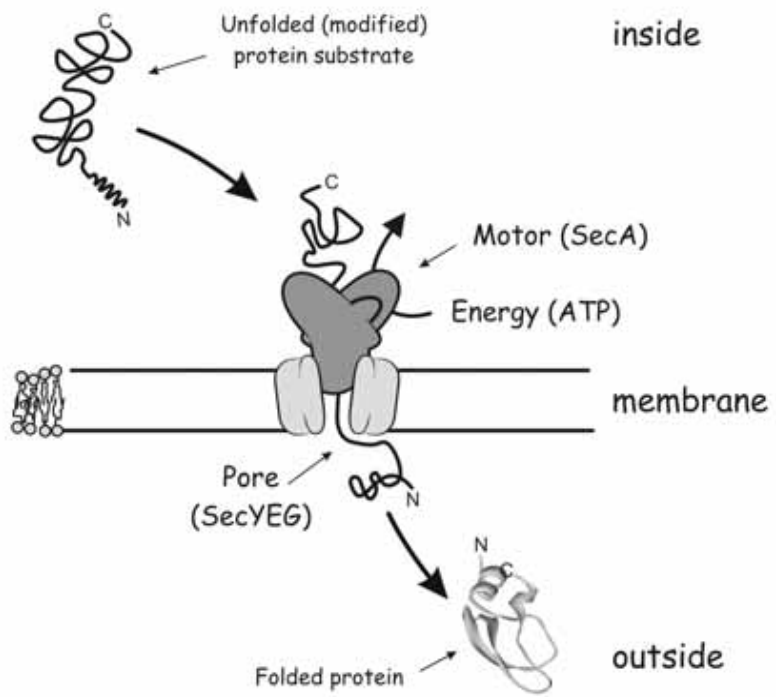


Does it work ?

Even better, look what we can do !

Why is this experiment important ?

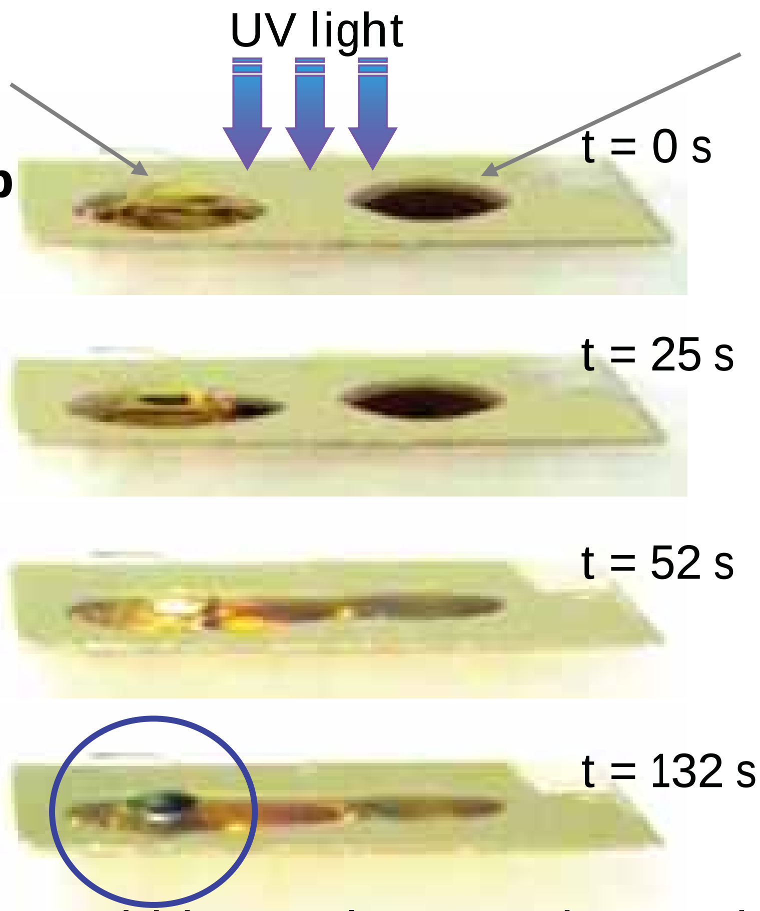
Demonstration of principle:
Biological motors are capable of transporting objects many times more massive than themselves



Possible application: Chemistry on a chip

Microfluidics: very tiny amounts of reagents (picolitre drops) moved with buffer liquids to react in very small volumes

Totally new possibilities if reagents can be moved without buffer liquid but with light.



Lateral view photographs of an acid-base colour reaction carried out on the photoresponsive surface**. Drops act as carriers of reagents and are transported towards each other by UV light, leading to the mixing of reagents. The product of reaction (blue) is formed in the static aqueous**

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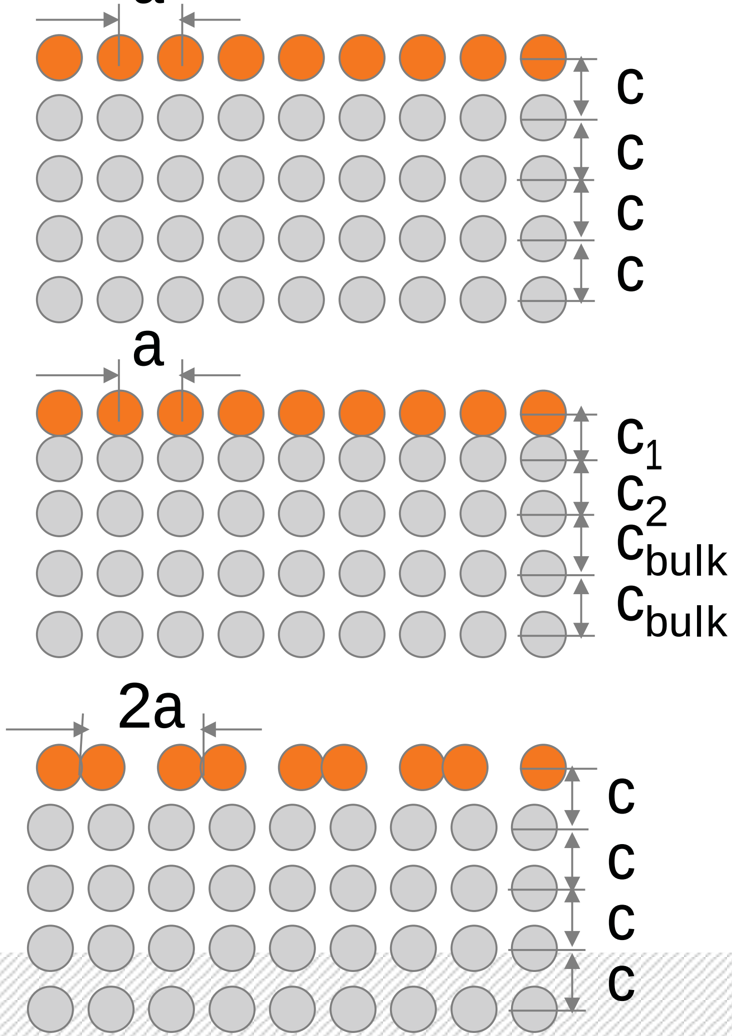
The surface was invented by the devil. *Wolfgang Pauli*



CLEAN SURFACES

IDEAL SURFACE

The terminating layer has the same atomic structure of an infinite crystal

RELAXATION

Rearrangement of the topmost layer(s) while preserving the periodicity parallel to the surface

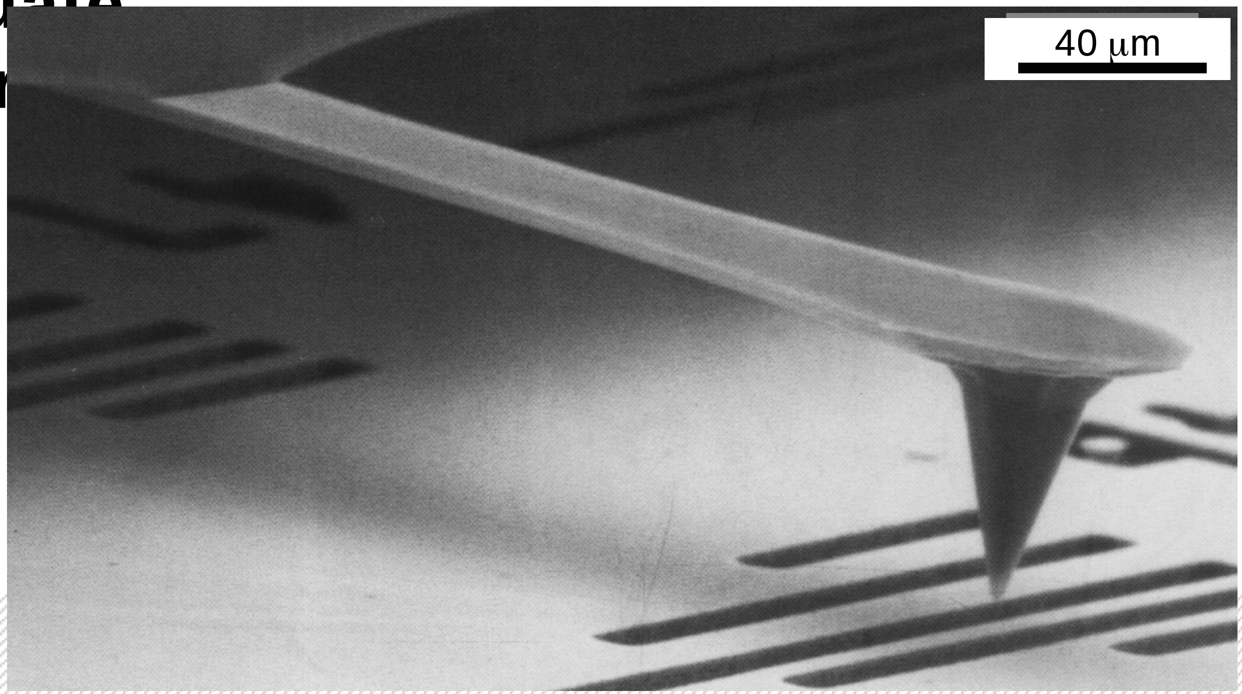
RECONSTRUCTION

Rearrangement of the topmost layer while breaking the periodicity parallel to the surface

Breakthrough: “see” and manipulate at the atomic scale

1981 Scanning tunneling microscopy developed by Gert Binning & Rohrer –Nobel Prize in 1986

Atomic Force Microscopy invented in 1986 by Gert Binnig, Calvin Quate, Christoph Gerber



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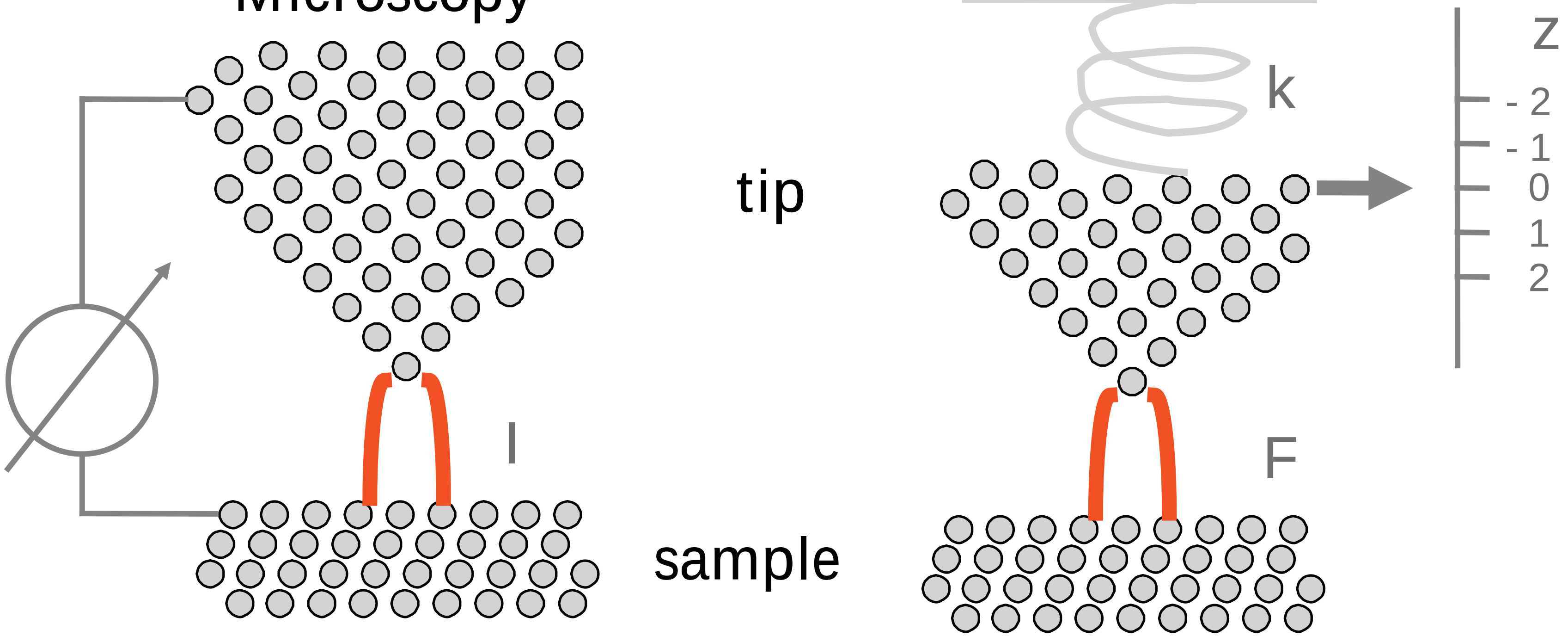
Scanning Microscopies

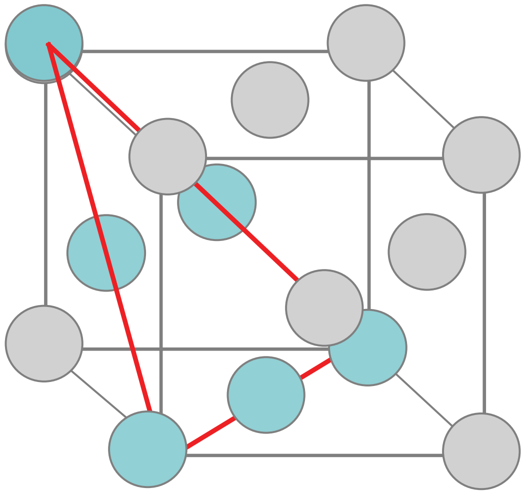
Scanning Tunneling Microscopy

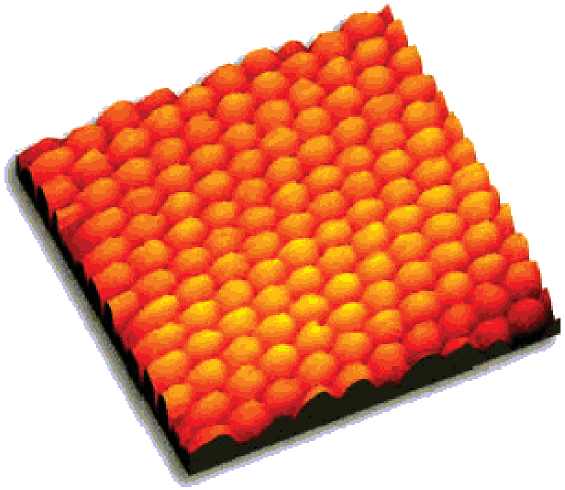
Scanning Force Microscopy



$$F = -k\,z$$

Scanning tunneling microscopy



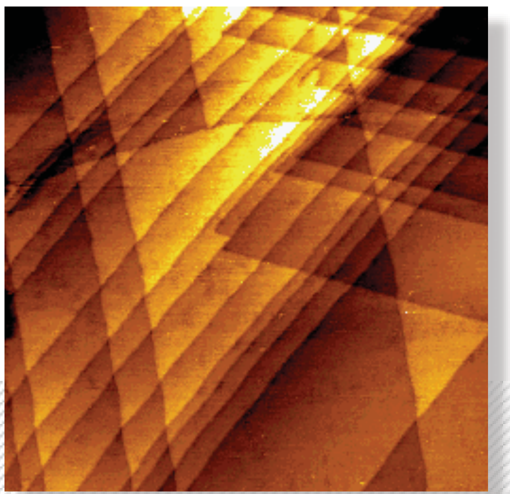


Au(111) surface

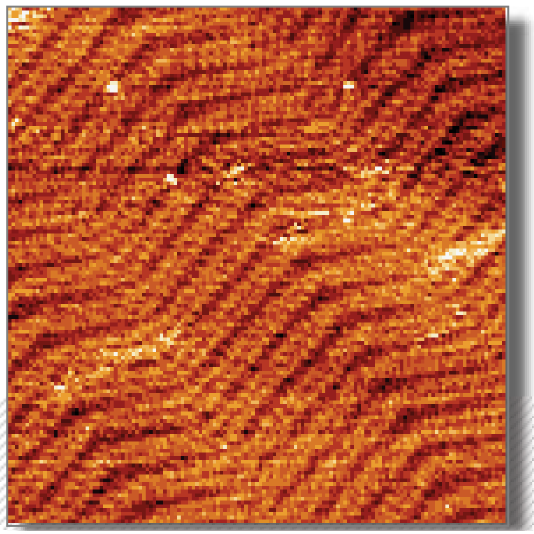
Atomic resolution (20 x 30 Å)

IBM STM picture gallery http://www.almaden.ibm.com/vis/stm/

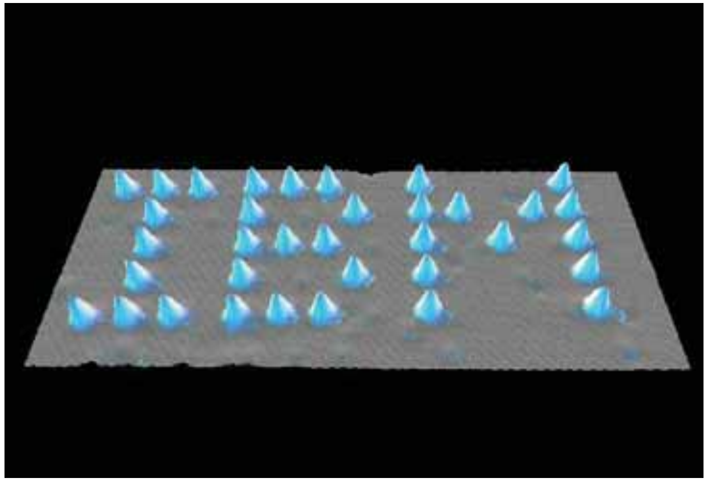
500×500 nm²



84×84 nm²



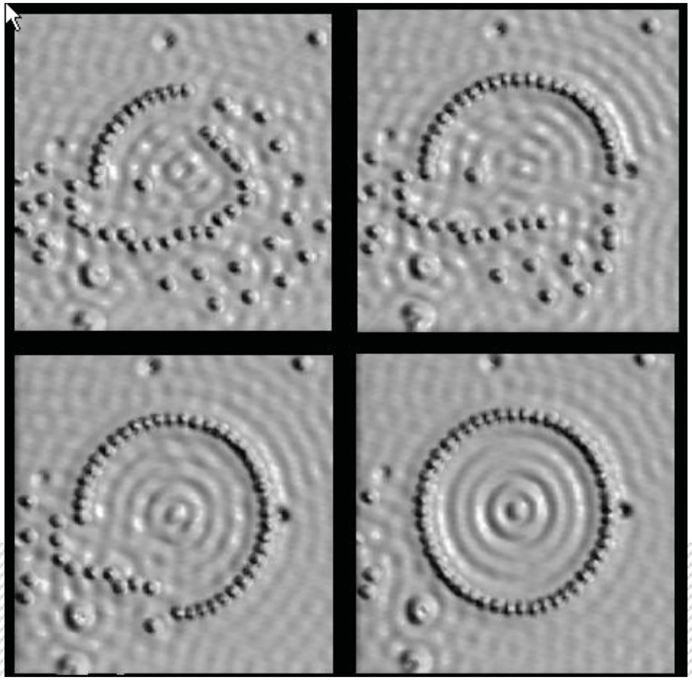
Scanning tunneling microscope can be used to displace atoms and molecules on surface



D.M. Eigler, E.K. Schweizer. Nature 344, 524-526 (1990).

Example:Xe/Ni

The tip of an STM is used to lift and put down the atomic units.



Example:Fe/Cu(111)

Quantum Corrals

One of the peculiar effects related to Quantum Corrals is the formation of a two-dimensional electronic gas (standing waves) confined within the corral.

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Atomic Force Microscopy (AFM)

Atomic resolution in contact mode on KBr

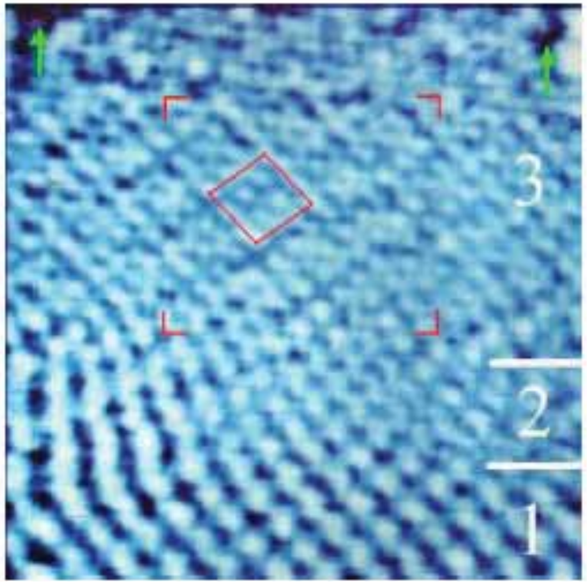


FIG. 20. (Color in online edition) Atomically resolved image of KBr (001) in contact AFM mode. Scan width of 5 nm in region 1, is continuously increased from 5 nm to 10 nm in region 2 and 10 nm in region 3 (see text). The $\sqrt{3}\times\sqrt{3}R45°$ superstructure and the slight depression in the central 5 nm $\times 5\ \mathrm{nm}^2$ area (enclosed by angles) is probably caused by the repulsive force of 1 nN between the front atom of the tip and the sample. The square shows the unit cell of the $\sqrt{3}\times\sqrt{3}R45°$ reconstruction; the arrows indicate atomic-size defects. From Giessibl and Binnig, 1992a.

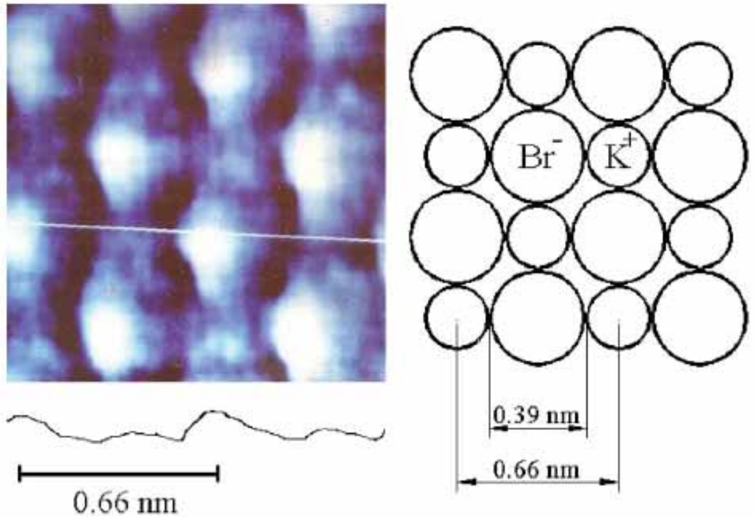
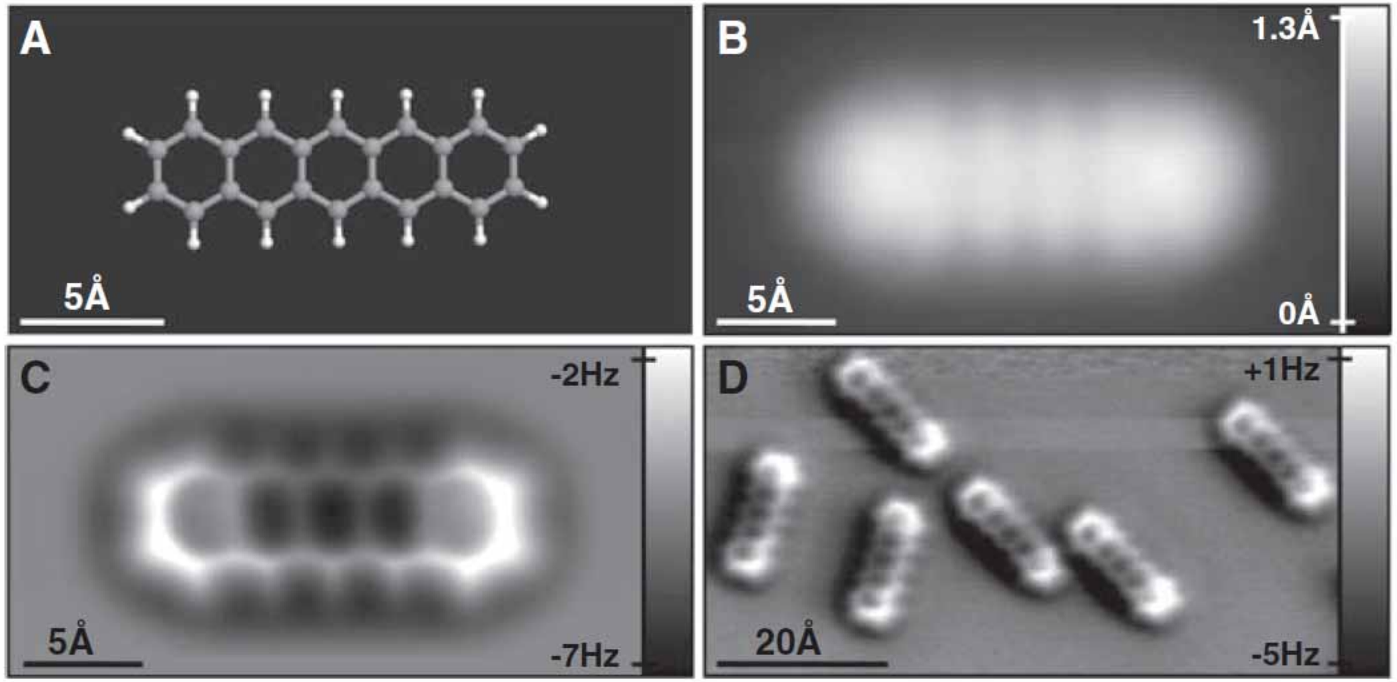


FIG. 19. (Color in online edition) Atomically resolved image of KBr (001) in contact AFM mode. The small and large protrusions are attributed to K^+ and Br^- ions, respectively. From Giessibl and Binnig, 1992b.

Atomic Force Microscopy



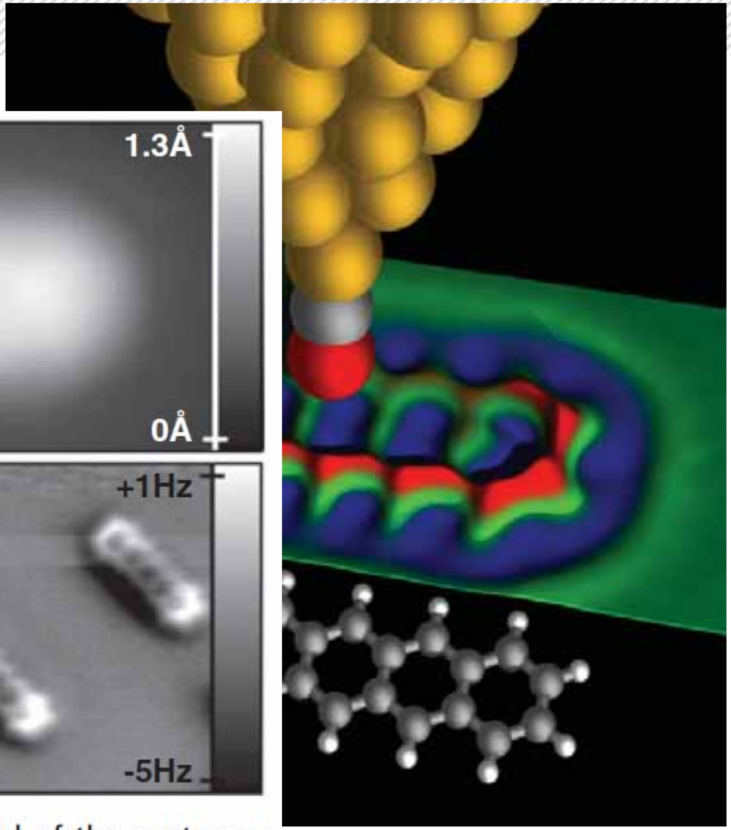


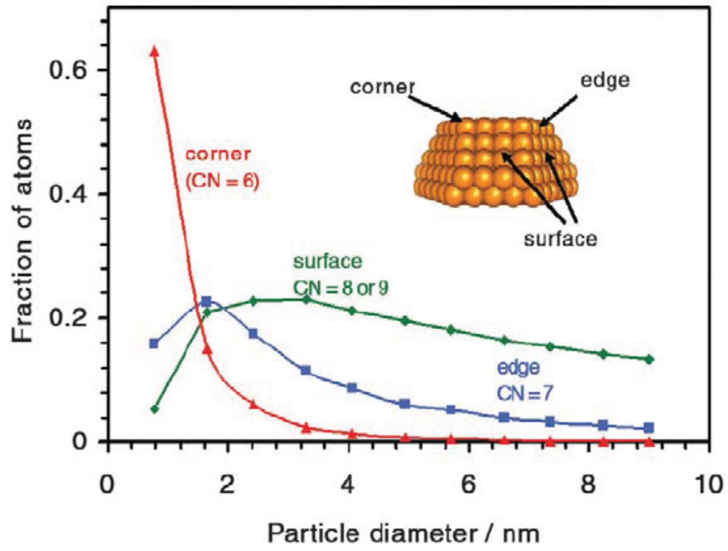
Fig. 1. STM and AFM imaging of pentacene on Cu(111). (**A**) Ball-and-stick model of the pentacene molecule. (**B**) Constant-current STM and (**C** and **D**) constant-height AFM images of pentacene acquired with a CO-modified tip. Imaging parameters are as follows: (B) set point $I = 110$ pA, $V = 170$ mV; (C) tip height $z = -0.1$ Å [with respect to the STM set point above Cu(111)], oscillation amplitude $A = 0.2$ Å; and (D) $z = 0.0$ Å, $A = 0.8$ Å. The asymmetry in the molecular imaging in (D) (showing a "shadow" only on the left side of the molecules) is probably caused by asymmetric adsorption geometry of the CO molecule at the tip apex.

Gross et al., Science 325 (2009) 1110

Surface atoms like to form bonds

The dissociative chemisorption energies for oxygen :

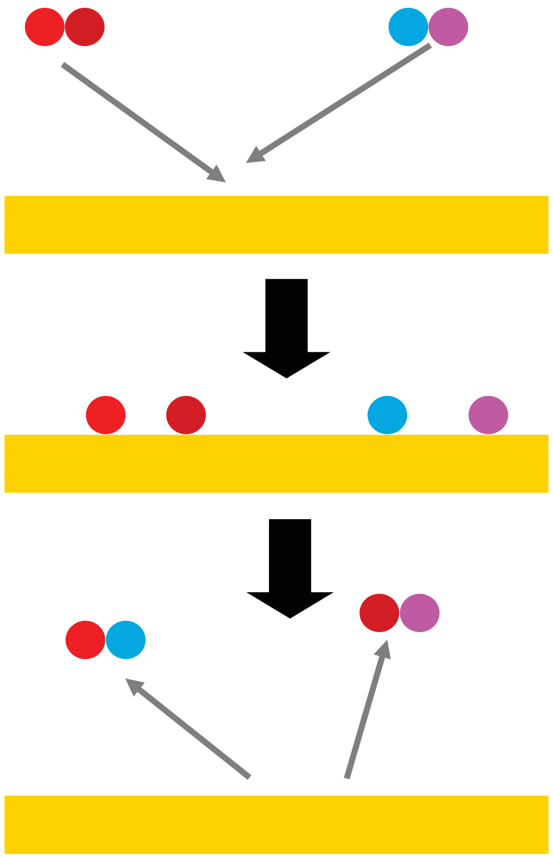
Cr	Mn	Fe -6,30	Co -5,07	Ni -3,90	Cu -2,51
Mo -7,48	Tc	Ru -4,62	Rh -4,03	Pd -1,20	Ag -0,65
W -8,62	Re	Os	Ir -4,65	Pt -2,17	Au +0,54



Britt Hvolbæk et al., Nanotoday 2007, 2, 14

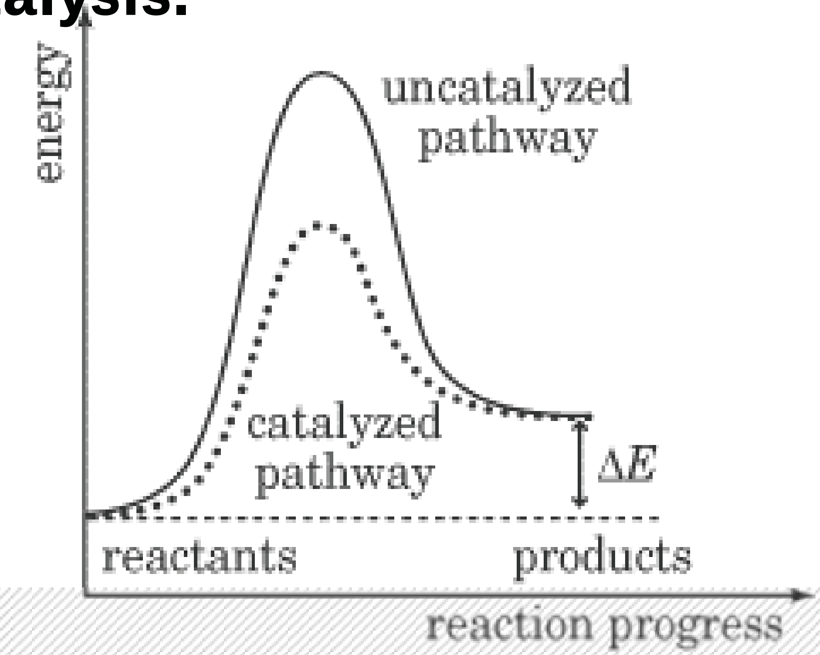
Due to extremely high surface area dust is explosive – even when macroscopic solid is not: ex. metal dust (Al, Mg), organic dust such as sugar, flour, paper, soap, plastics, wood, coal

Positive side: catalysts



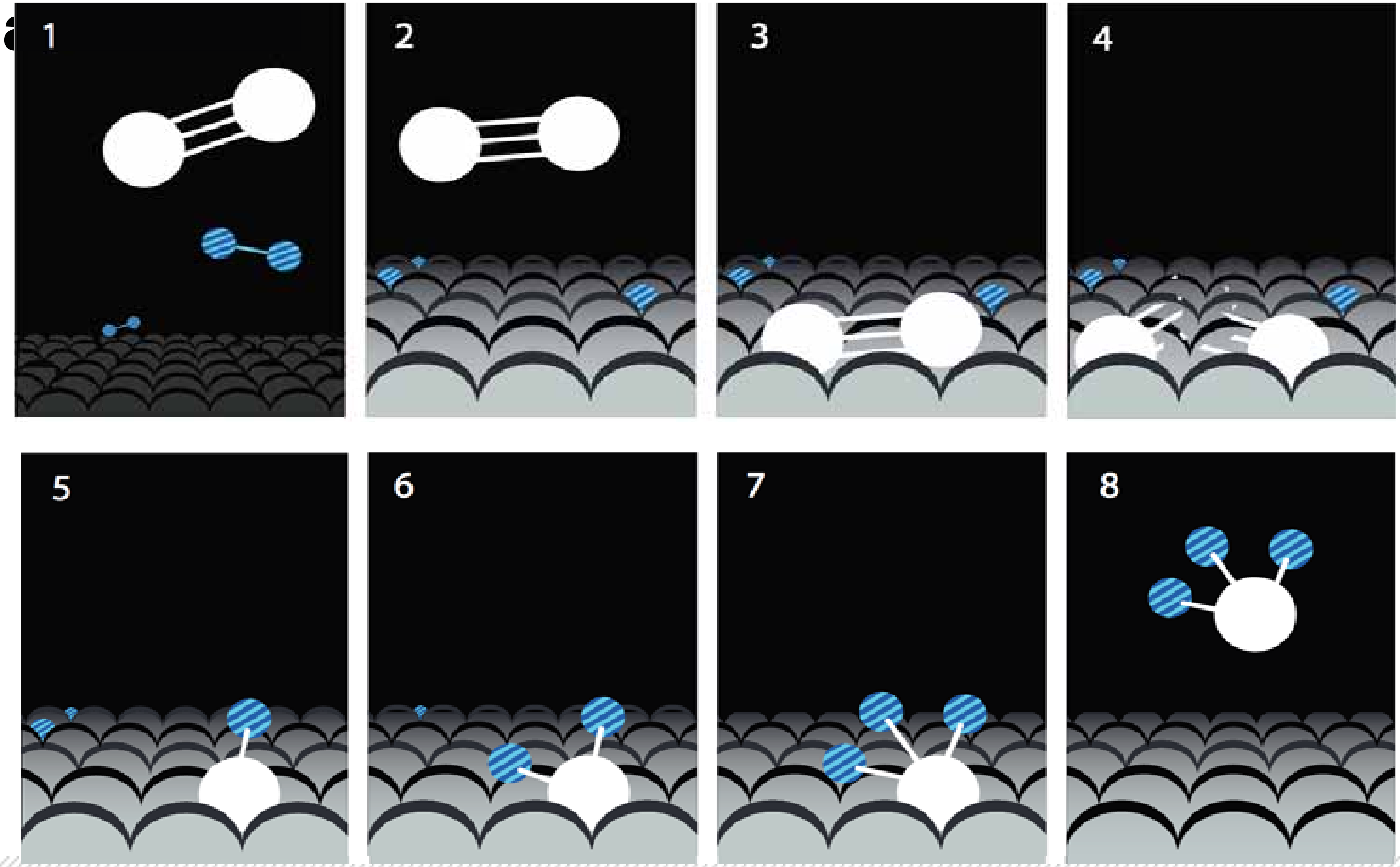
The catalyst initiates or accelerates a chemical reaction without itself being affected.

20% of the gross national product (GNP) of industrial countries relies in one way or another on catalysis.



Gerhard Ertl - Nobel Prize in Chemistry 2007

Haber-Bosch-process: **N2 reacts with H2 to form a**

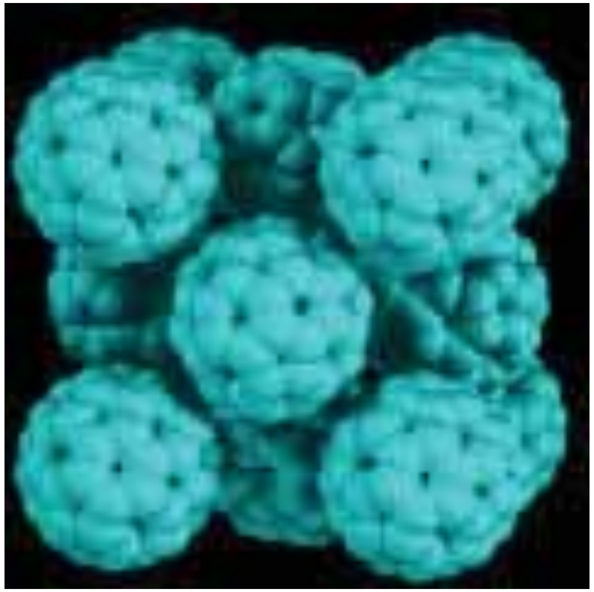


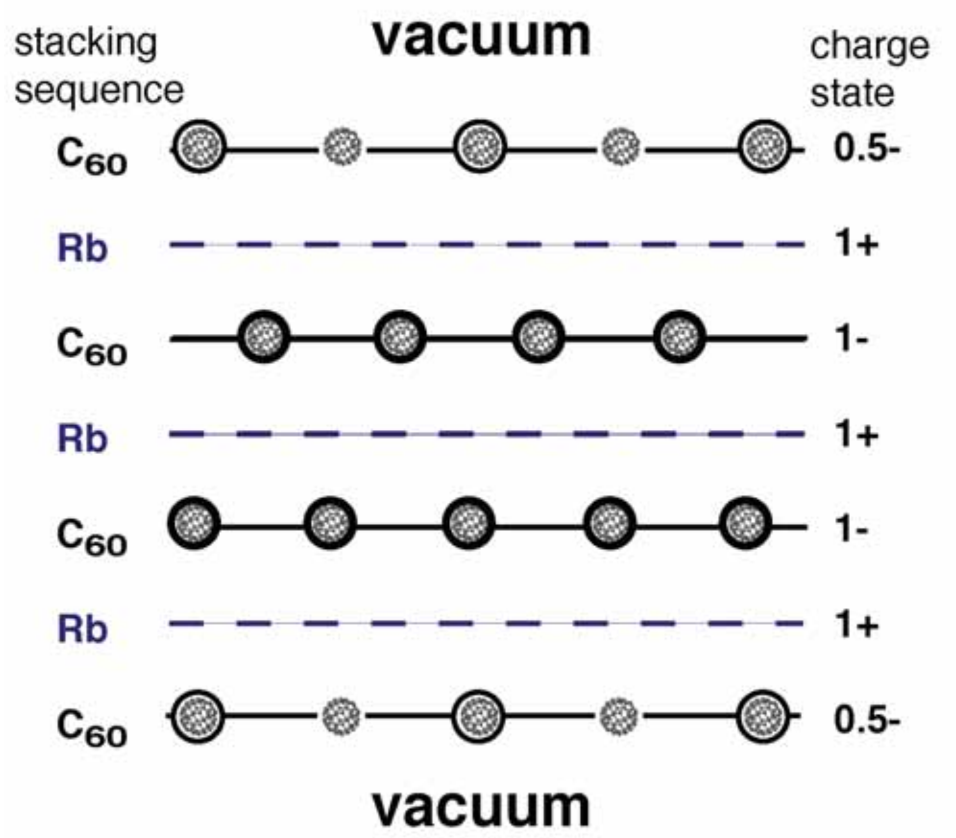
G.Ertl, Primary Steps in Catalytic Synthesis of Ammonia. J.Vac.Sci.& Tech. A 1(2) 1247–1253 (1983)

The Nobel Prize in Chemistry 2007, the Royal Swedish Academy of Sciences, www.kva.se

Charge reconstruction at the surface of polar solids

C_{60}



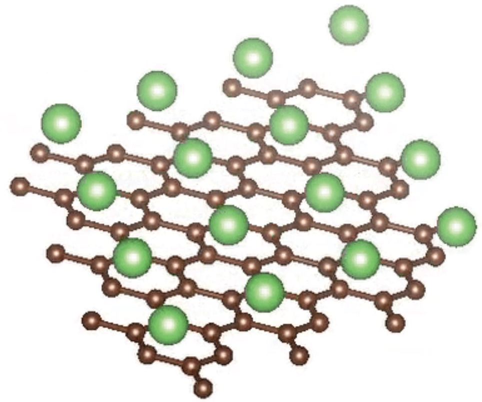


To resolve polar instability, surface e⁻ density reduced to ½ that of bulk e⁻ localized on single molecules ⇒ Surface layer: 50%C_{60} + 50%$(C_{60})^-$

Surfaces and very thin films where electrons are highly correlated

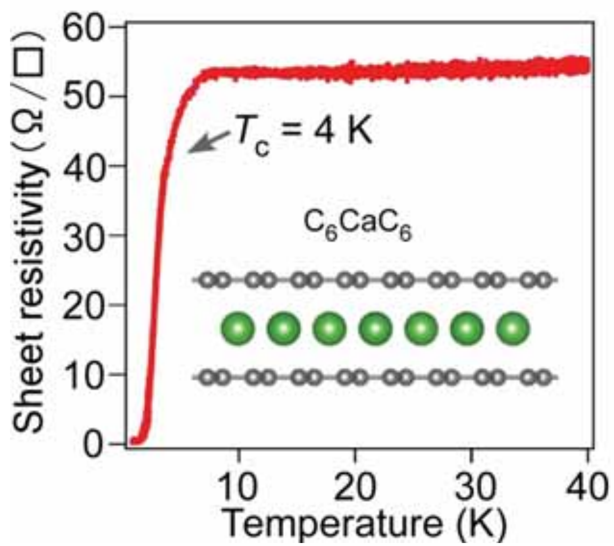
Superconductivity in atomically thin materials

In recent years superconductivity was found in diverse monolayers:



•**The first: metallic monolayers (*e.g*. lead)**

•**Alkali-decorated graphene:**
T_c ~ 1 – 6 K.



G. Profeta *et al*., Nat. Phys. 8, 131 (2012); B. M. Ludbrook *et al*., Proc. Natl. Acad. Sci. 112, 11795 (2015); S. Ichinokura *et al*., ACS Nano 10, 2761 (2016)

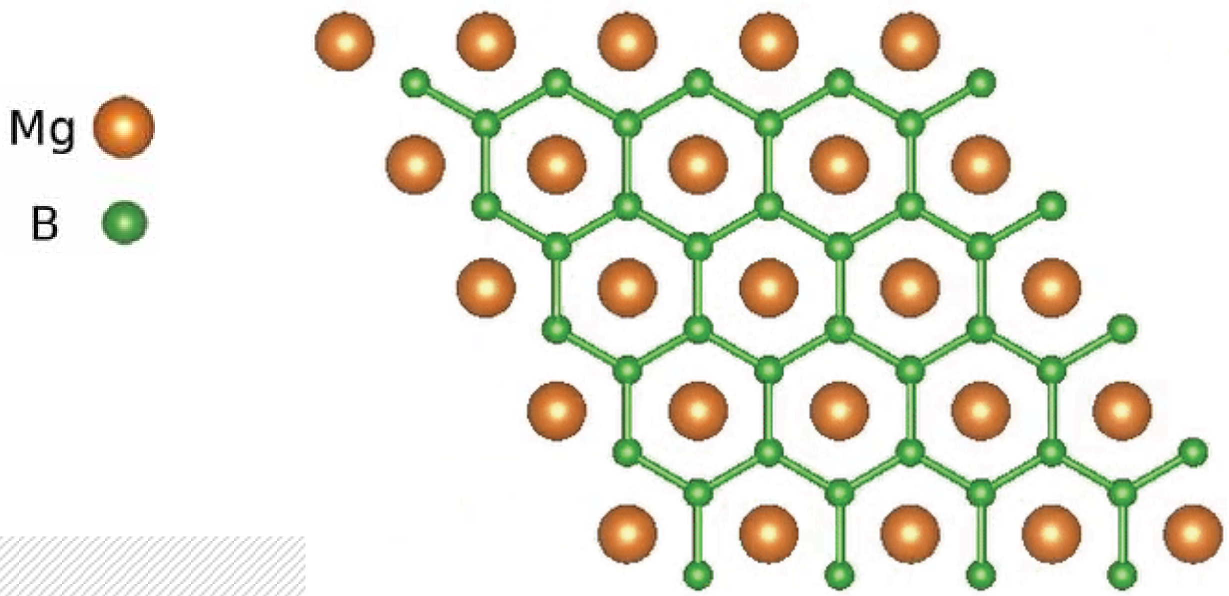
› Superconductivity in monolayers not only possible, but even ideal for stronger and enriched superconductivity on nanoscale.

Known bulk superconductor with T_c = 39 K:

magnesium diboride (MgB_2)

carbon ⇒ boron

lithium ⇒ magnesium

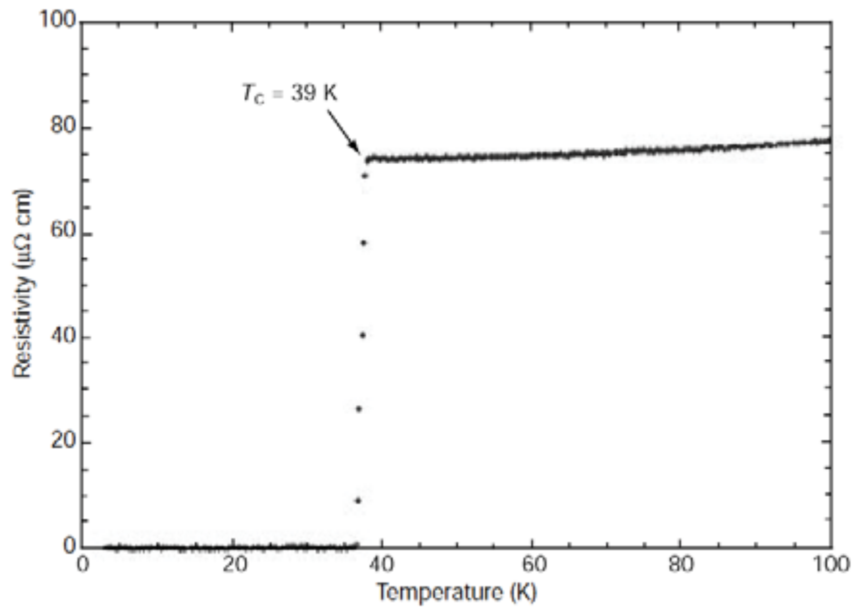


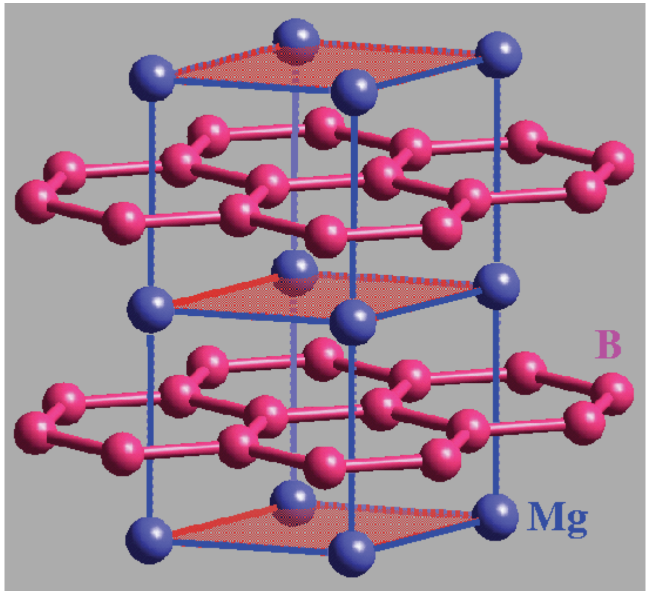
MgB_2

Superconductivity at 39 K in magnesium diboride

Jun Nagamatsu*, Norimasa Nakagawa*, Takahiro Muranaka*, Yuji Zenitani* & Jun Akimitsu*†

NATURE | VOL 410 | 1 MARCH 2001





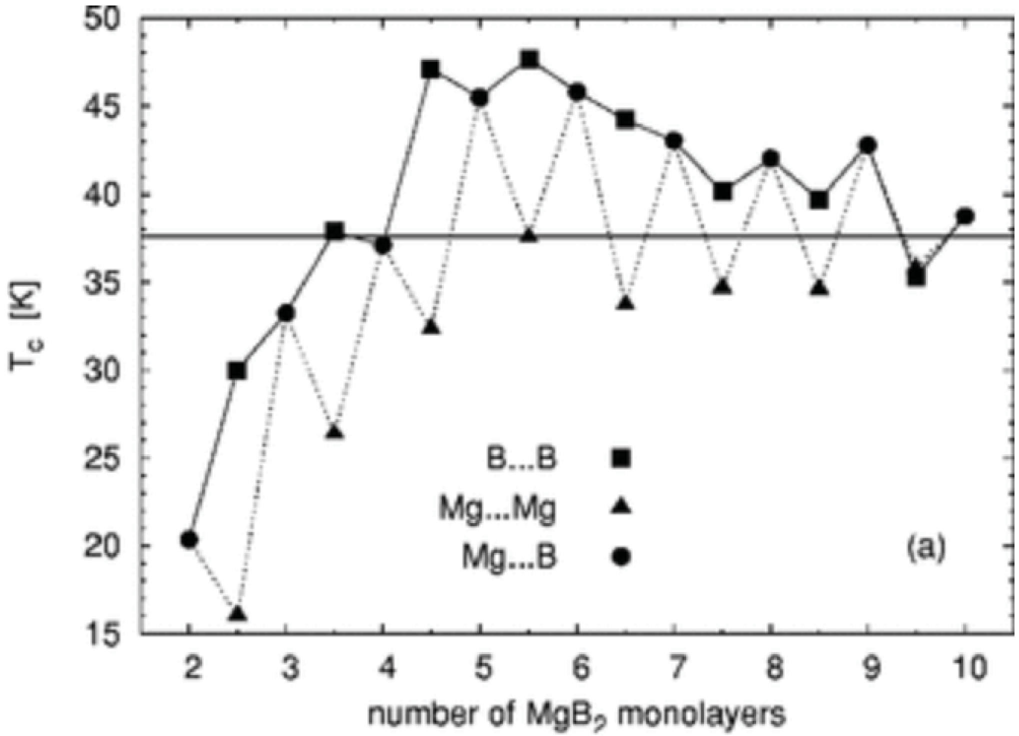
What happens when we make the material only a few layers thick?

Superconductivity observed for thicknesses 6 layers and higher

What happens for MgB2 thin films?

Quantum size effects are expected to give rise to oscillations in Tc with thickness

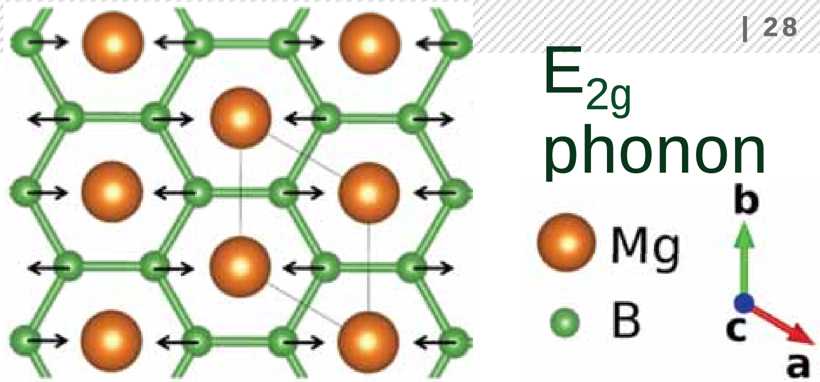
Critical temperature of MgB2 ultrathin superconducting films: BCS model calculations in the tight-binding approximation Karol Szałowski, Physical Review B 74, 094501 (2006)

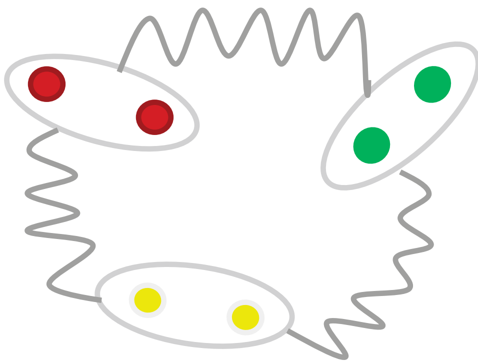


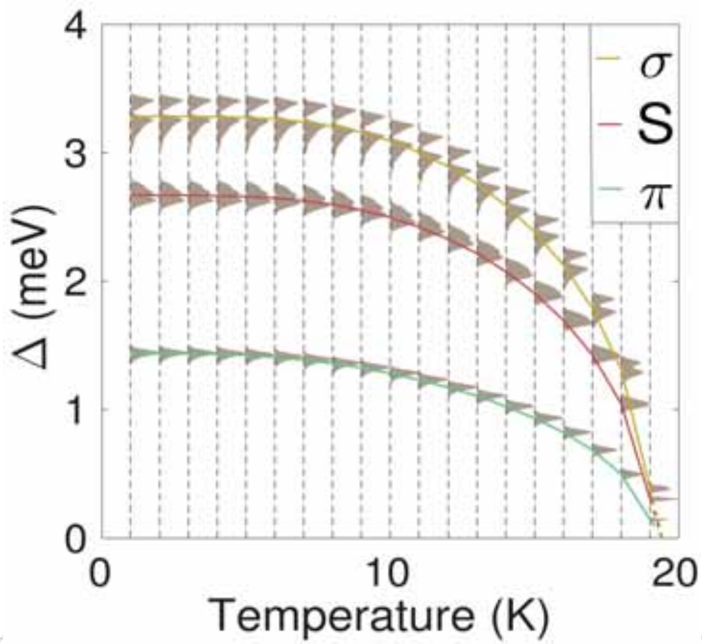
We saw nothing like that !

Three-gap superconductivity in monolayer MgB_2

- Mediated by phonons.
- Three different Cooper-pairs with different Δ's.
- Coupling between Cooper-pair condensates enhances T_c : 20 K.





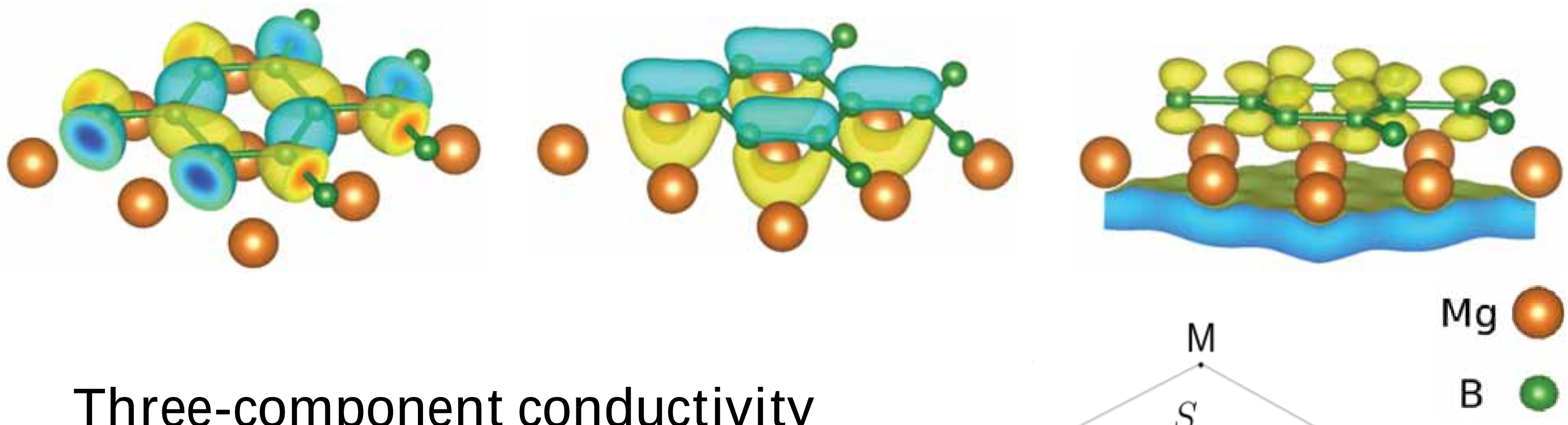


Jonas Bekaert *et al*., Phys. Rev. B 96, 094510 (2017); Jonas Bekaert *et al*., Sci. Rep. 7, 14458 (2017)

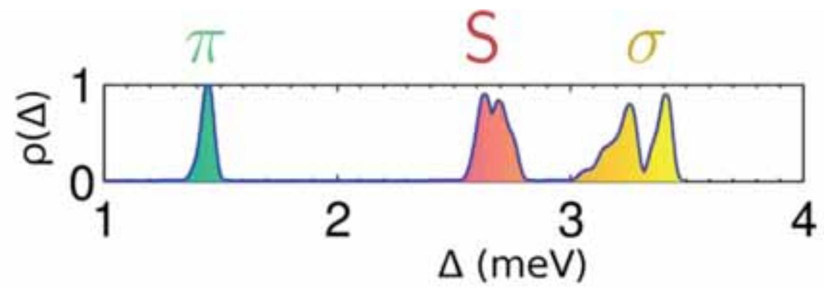
Three-gap superconductivity in ML MgB_2

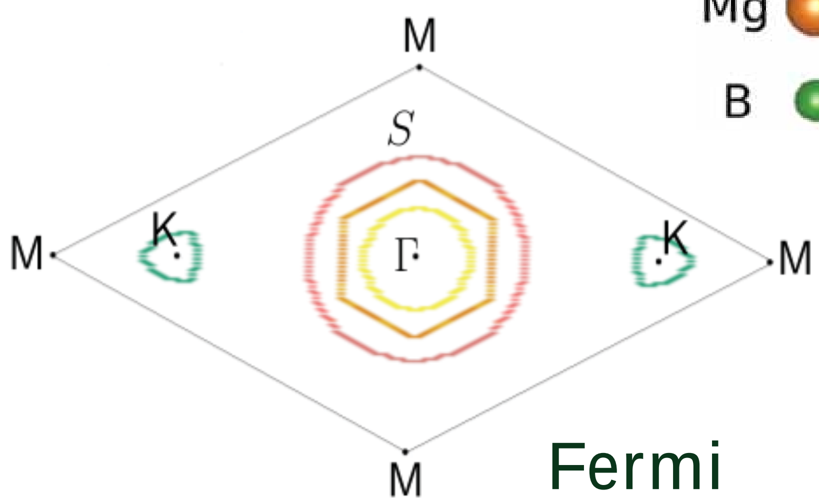
- Three very different electronic states:

σ: π: Surface state (S):



Three-component conductivity

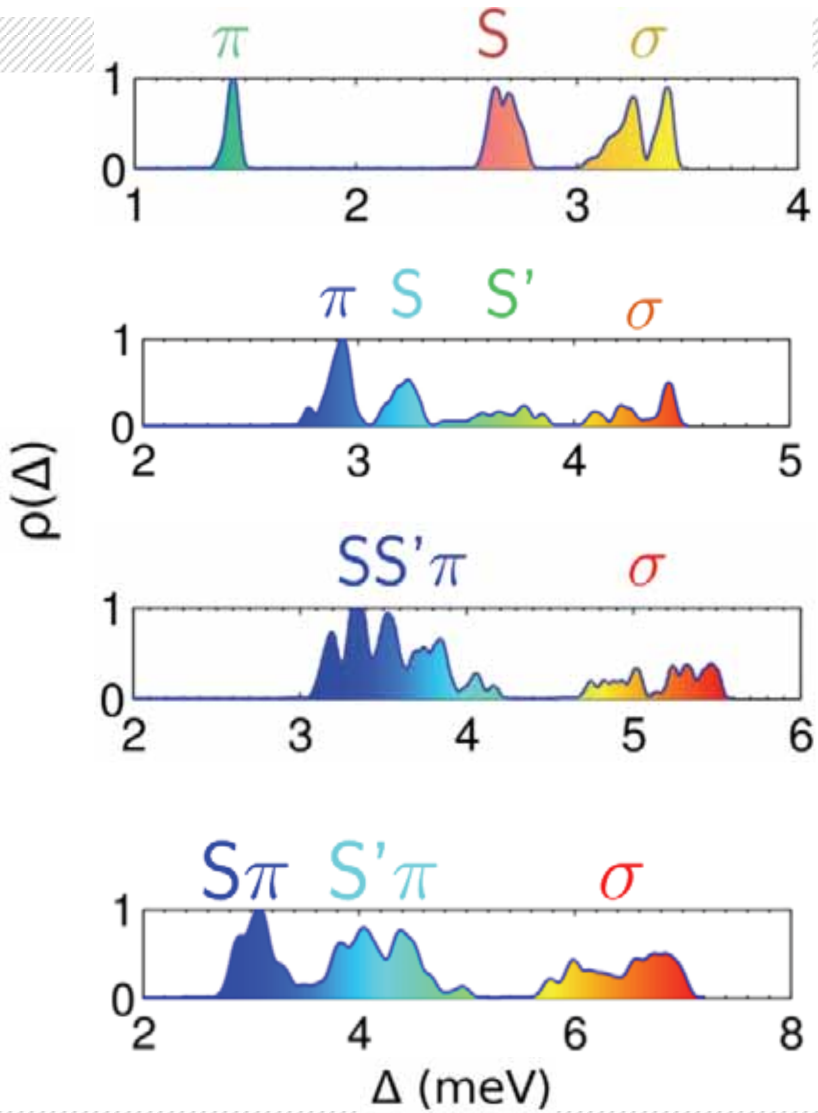




Fermi surface

J. Bekaert *et al.*, Phys. Rev. B 96, 094510 (2017); J. Bekaert *et al.*, Sci. Rep. 7, 14458 (2017)

Evolution of multigap spectrum of MgB_2 with added layers



1 ML

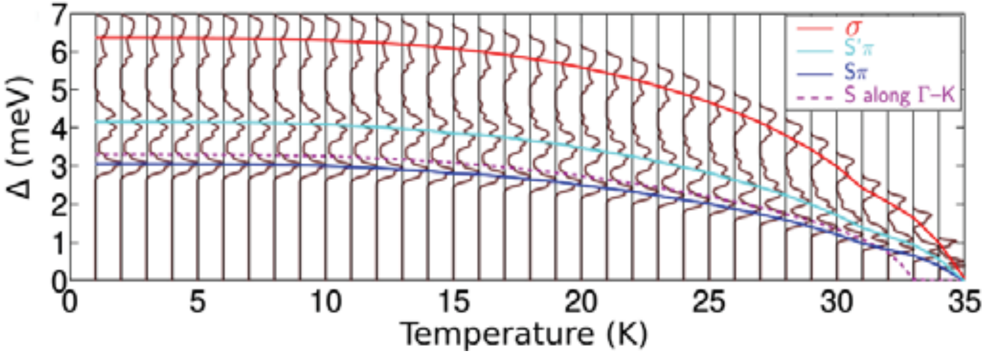
2 M

4 ML

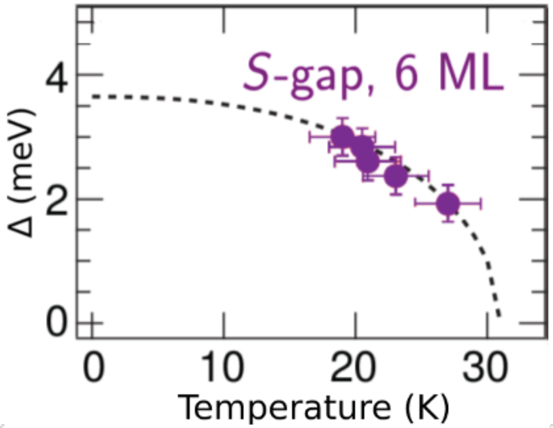
6 ML

6-ML sample:

Theory



Experiment



Jonas Bekaert *et al.*, Phys. Rev. B 96, 094510 (2017); Jonas Bekaert *et al.*, Sci. Rep. 7, 14458 (2017)

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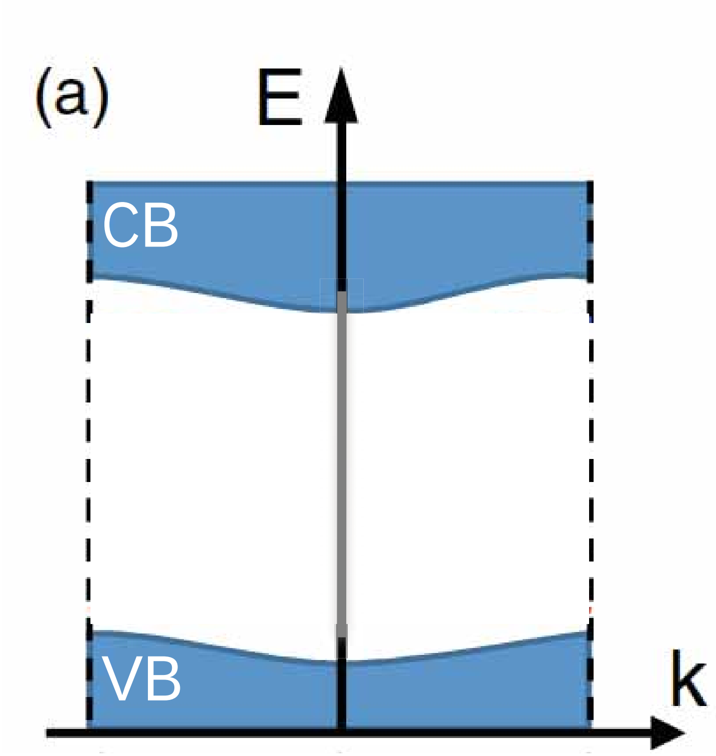
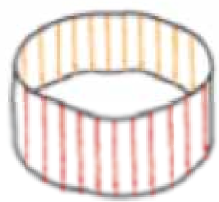
For electrons at surfaces other special things can happens to....

- VB = *valence band*; CB = *conduction band*



Normal insulator



crystal momentum, k

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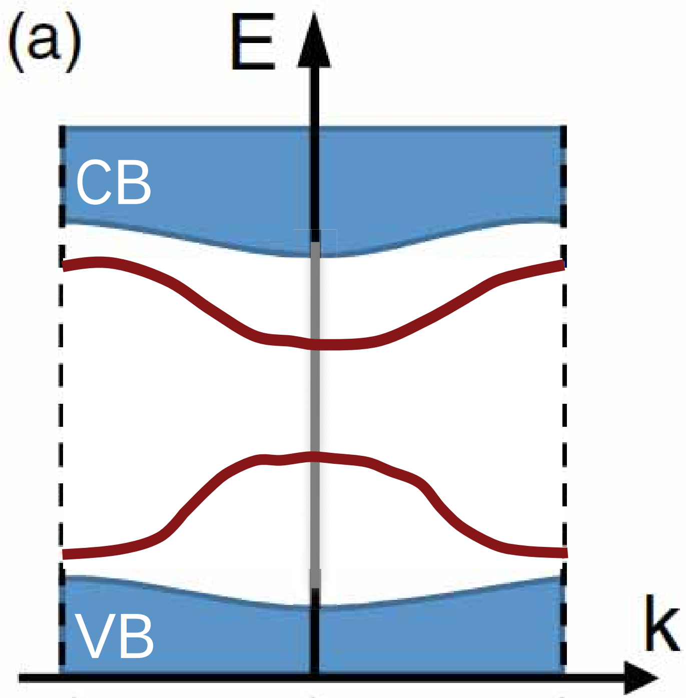
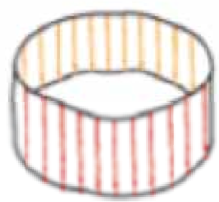
- one can have states (bands) in the gap

→ *e.g. due to surface states*

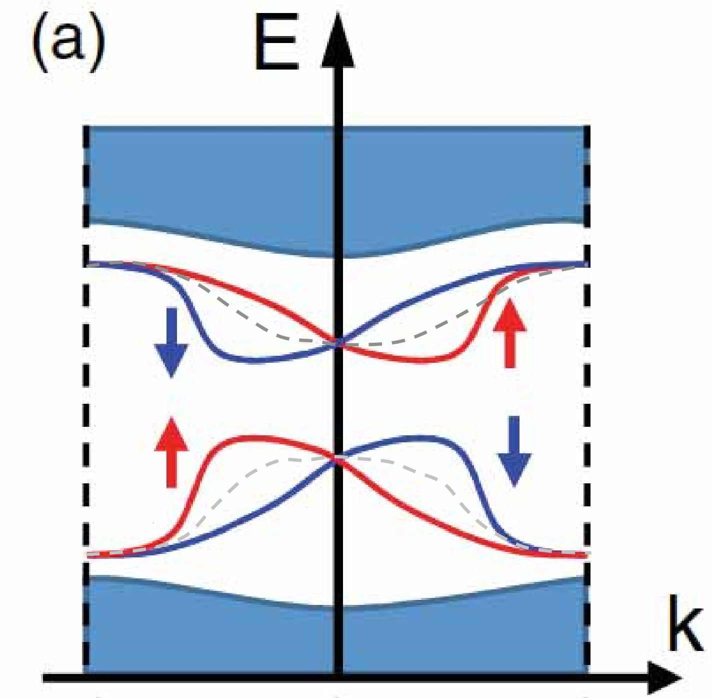


Normal insulator with in-gap states

crystal momentum, k

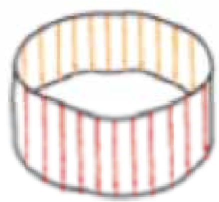


- energies for spin up and spin down eigenstates not equal → *e.g. due to spin-orbit coupling*



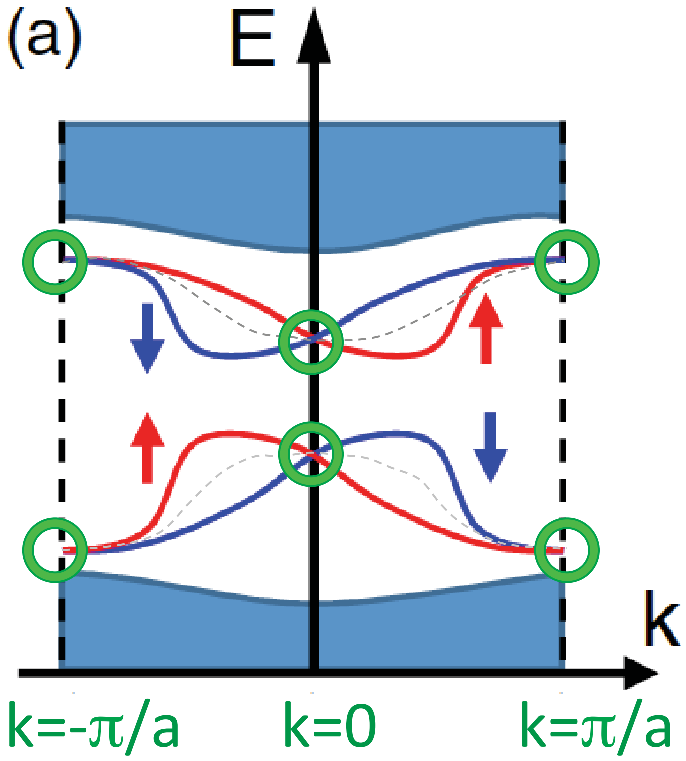
crystal momentum, k

In-gap states can be spin-polarized



Kramer's theorem

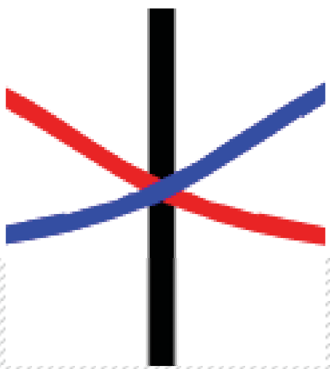
- time reversal invariance
- fermions (half-integer spin)

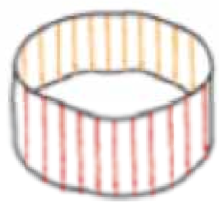


crystal momentum, k

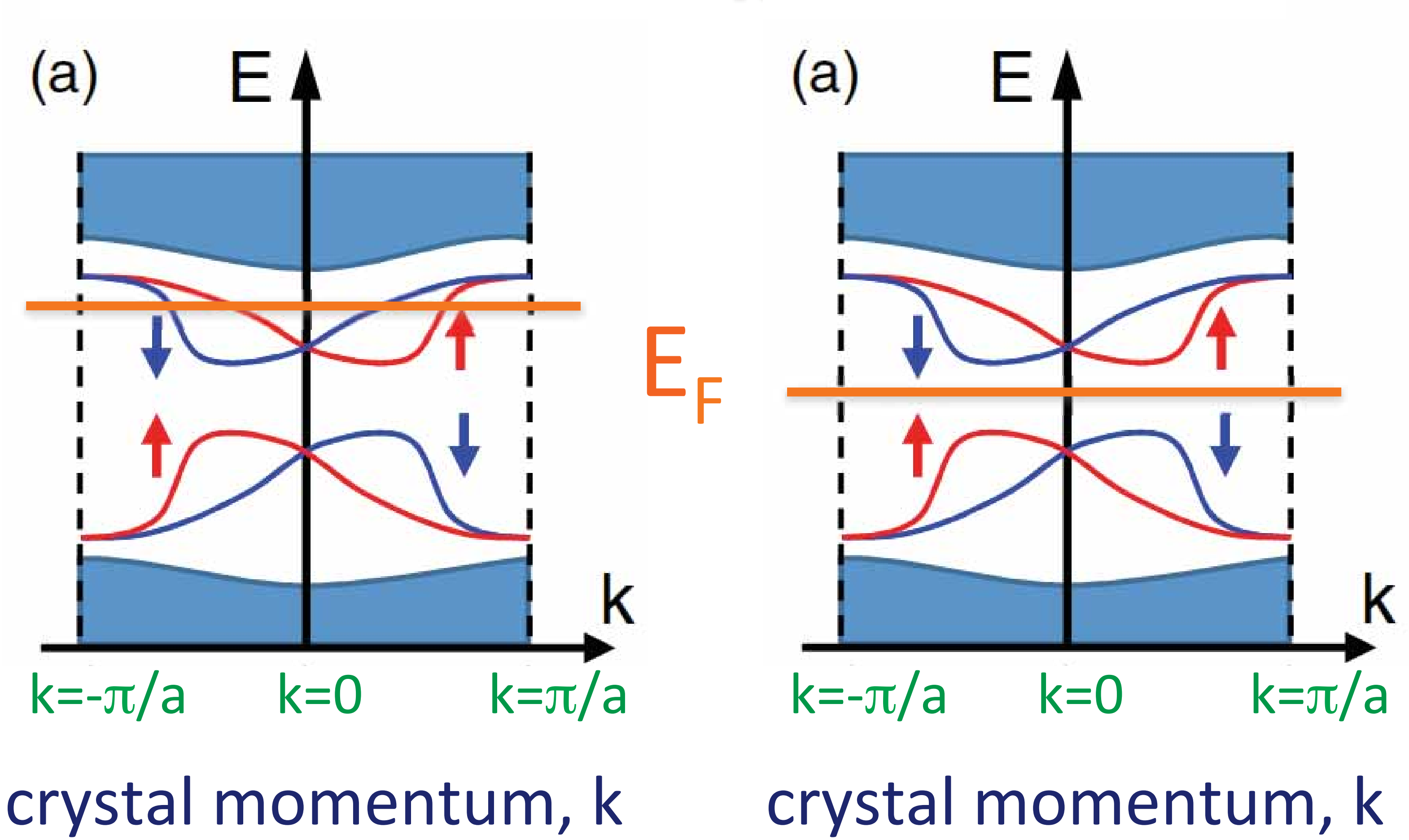
at Kramers points
(TRI momenta)

more than one eigenstate
has to have the same energy





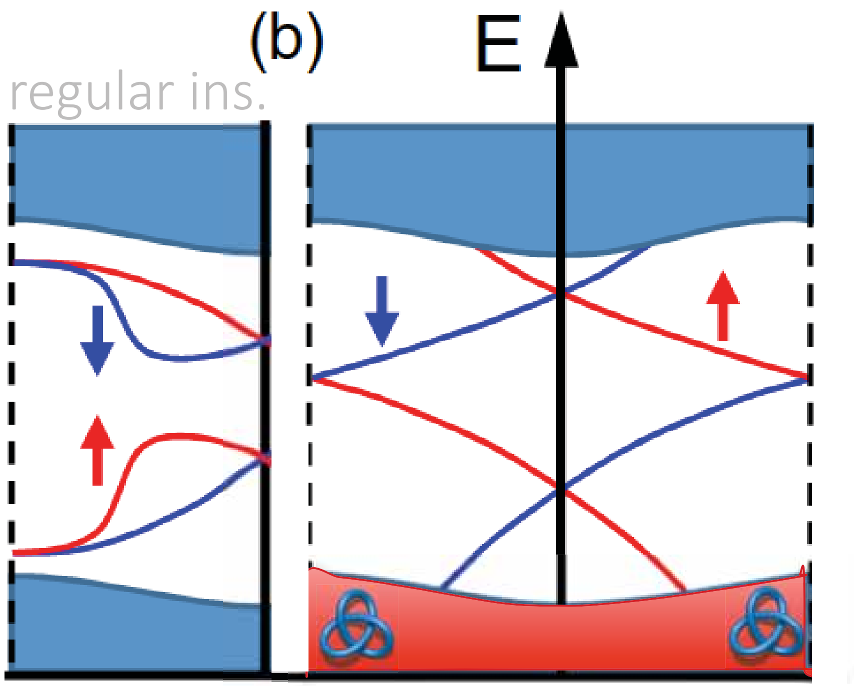
adiabatic deformation → E_{Fermi} can lie in the gap



these metallic surface states are **not protected**

Topological insulators

- totally different kind of surface states

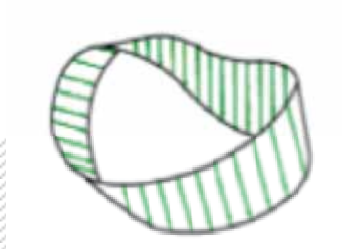


k=-π/a k=0 k=π/a

crystal momentum, k

they have to be there

as long as TRI
they have to be metallic



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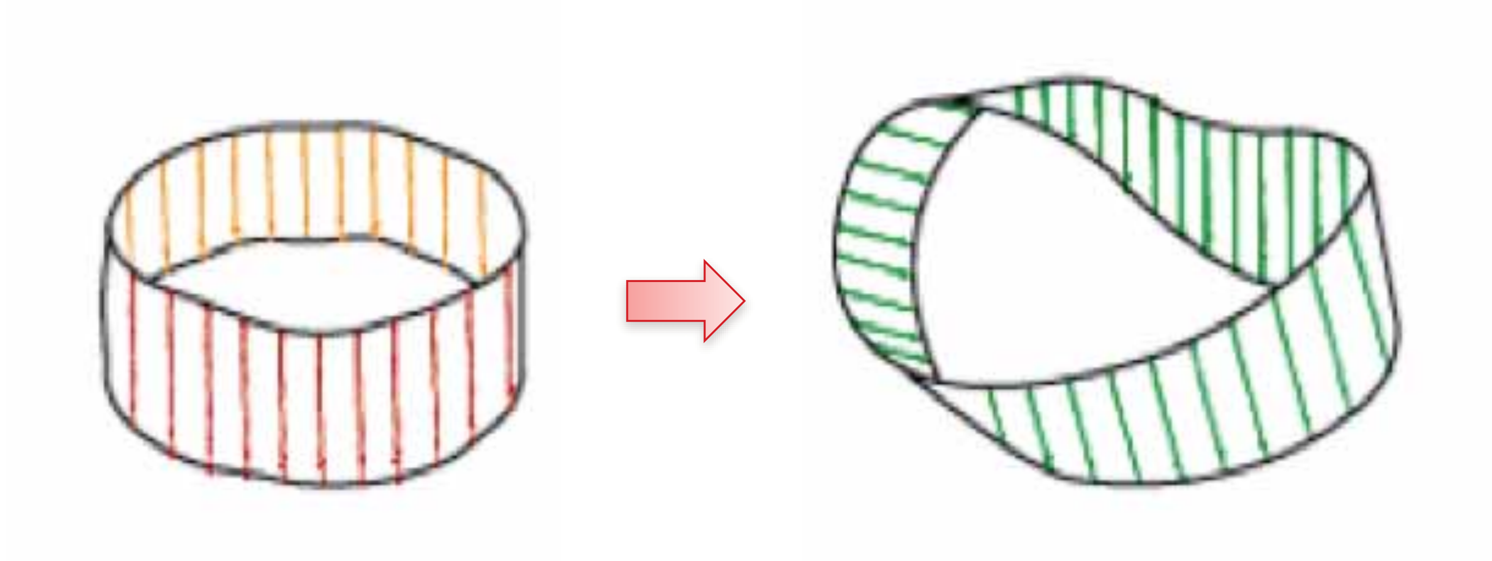
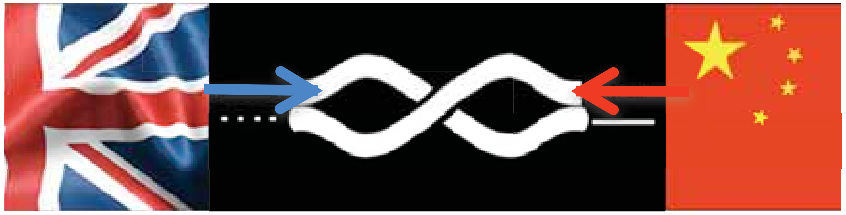
Topology of the bulk

- this means if we can make the bulk topologically non-trivial (e.g. $Z_2 = 1$ rather than 0)

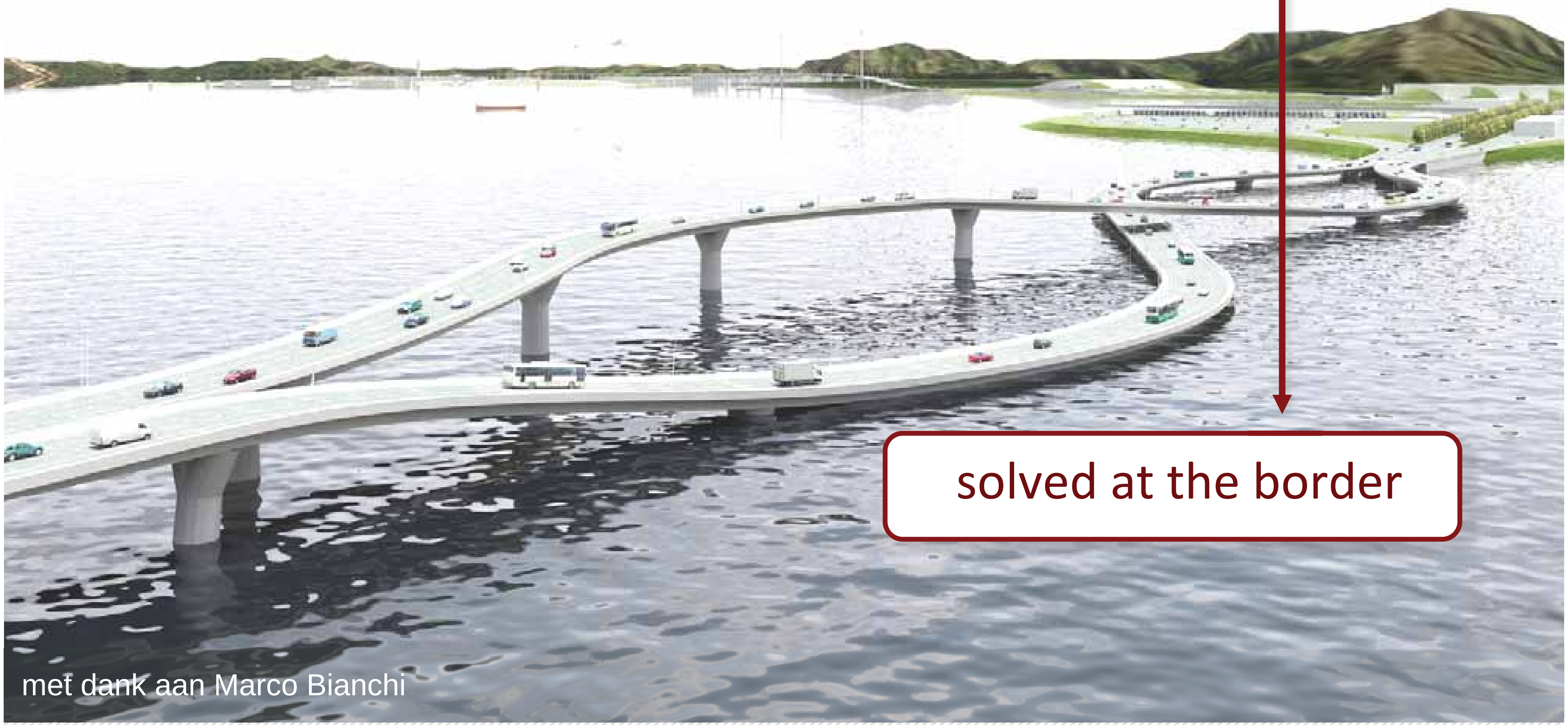


- something special has to happen at the boundary of the system, and that something is protected


Map
Sat
Ter
Earth
Huizhou
Dongguan
Shenzhen
Hong Kong
Kwun Tong
right
left

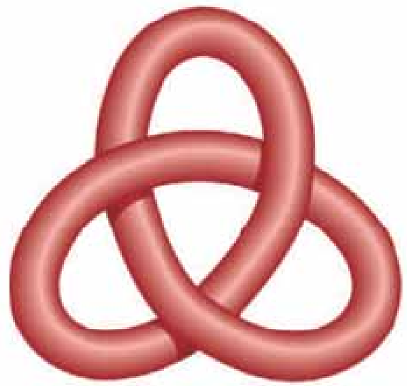


inland property

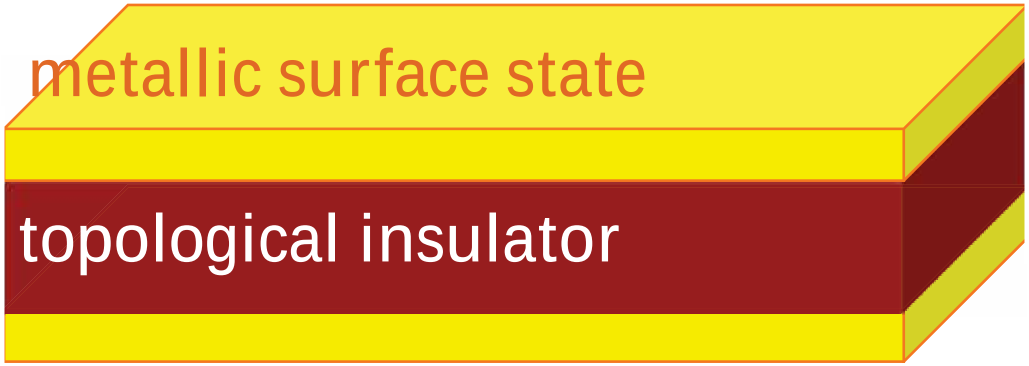


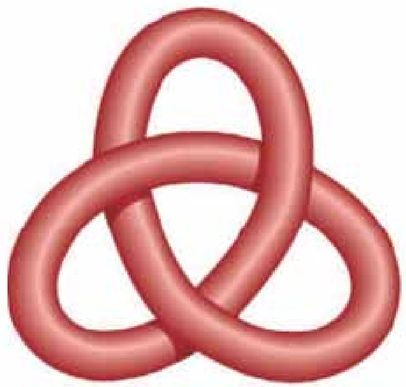
solved at the border

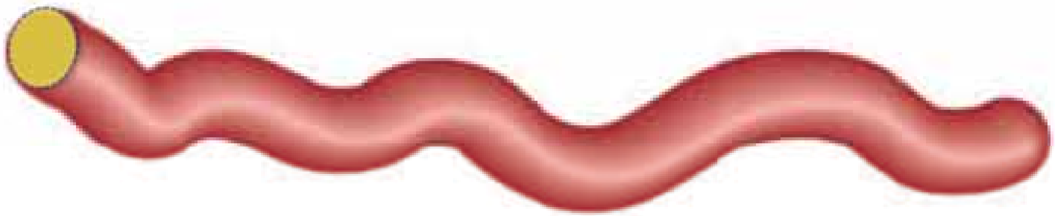
Surface electronic states are very different




insulator


metallic surface state
topological insulator





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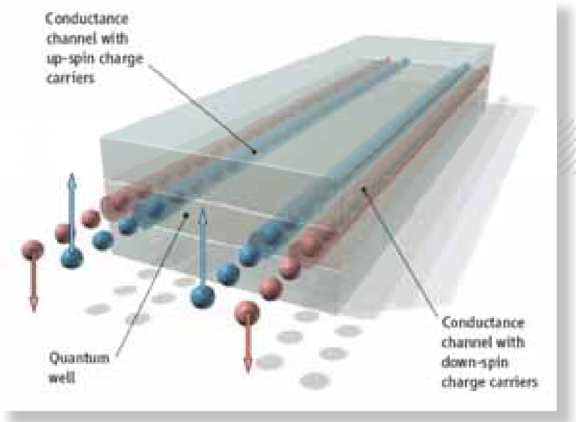
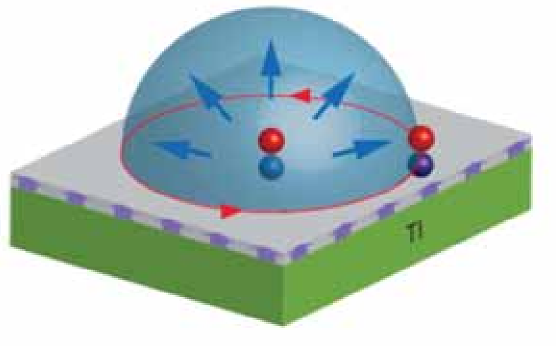
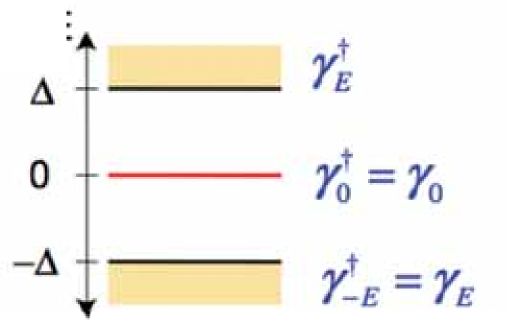
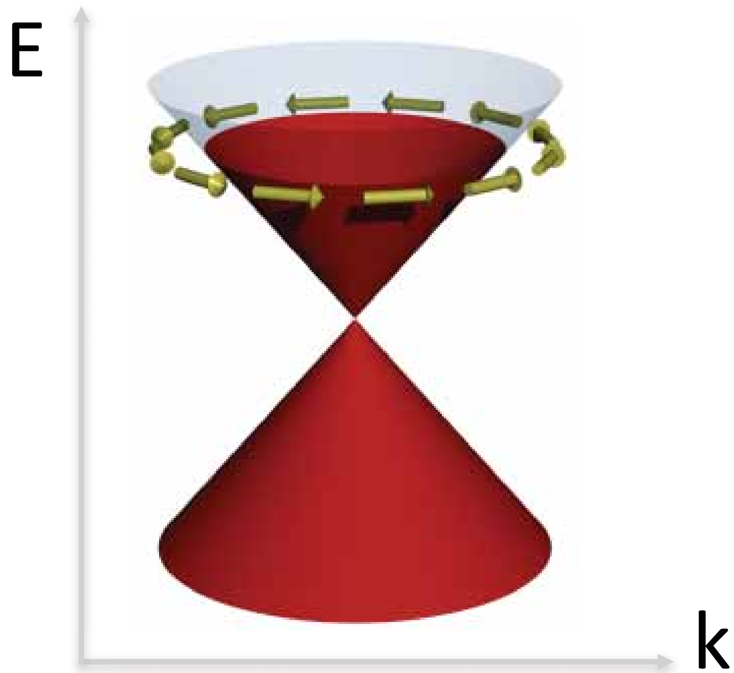
- 100% spin polarised states for (low energy) spintronics
- quantum spin Hall effect
- magnetic monopoles
- Majorana zero modes

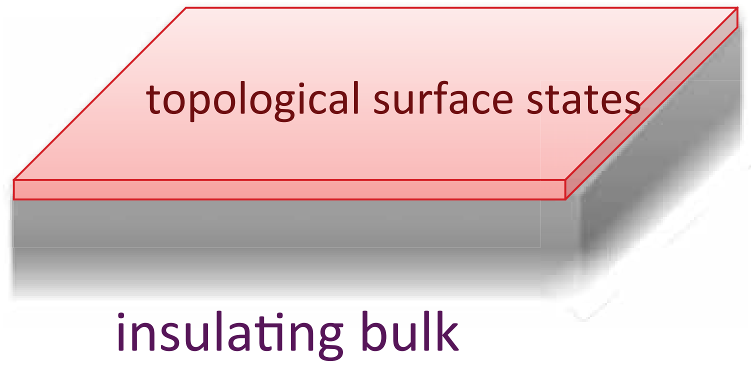






- topologically protected surface states with linear dispersion → Dirac cone

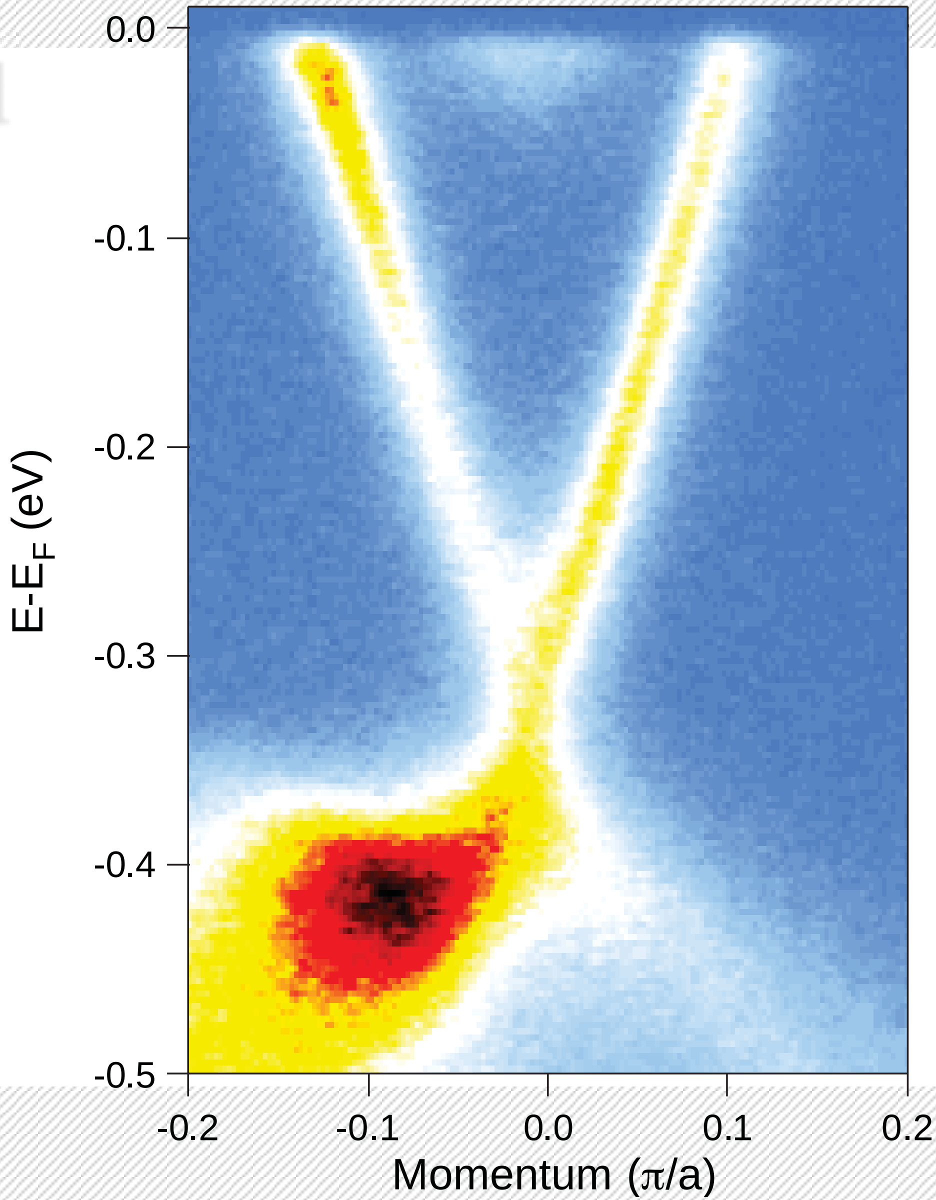




Bi_2Te_2Se – starts to look like the business...

- Dirac cone confirmed
- very few 'in cone' states
- high resistivity, bulk insulating behaviour

Mark Golden's group in Amsterdam



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Thank you for your attention!