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ICTP 40th Anniversary

SMR 1564 - 33

SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
(24 May - 11 June 2004)

NANOSCALE SURFACE PHYSICS WITH LOCAL PROBES:
(i) Two-dimensional self-assembly of supermolecules and of atomic superlattices; (ii) Insulators at the limit
PART II

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These are preliminary lecture notes, intended only for distribution to participants.

Nanoscale Surface Physics with Local Probes: Electronic Bandstructure of a Two-Dimensional Self-Assembled Adatom Superlattice

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Ecole Polytechnique Fédérale de Lausanne, Switzerland

M. Ternes, M. Pivetta, F. Silly, F. Patthey, J. P. Pelz,
C. Weber, Th. Giamarchi, F. Mila

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Definition

Self-assembly is the autonomous organisation
of
components
into
patterns or structures
without
human intervention

G. M. Whitesides, B. Grzybowski, Science **295**, 2418 (2002)

Fig. 1. Examples of static self-assembly. (A) Crystal structure of a ribosome. (B) Self-assembled peptide-amphiphile nanofibers. (C) An array of millimeter-sized polymeric plates assembled at a water/perfluorodecalin interface by capillary interactions. (D) Thin film of a nematic liquid crystal on an isotropic substrate. (E) Micrometer-sized metallic polyhedra folded from planar substrates. (F) A three-dimensional aggregate of micrometer plates assembled by capillary forces. [Image credits: (A) from (*24*); (B) from (*25*); (C) from (*26*); (D) from (*27*); (E) from (*28*); (F) from (*29*)]

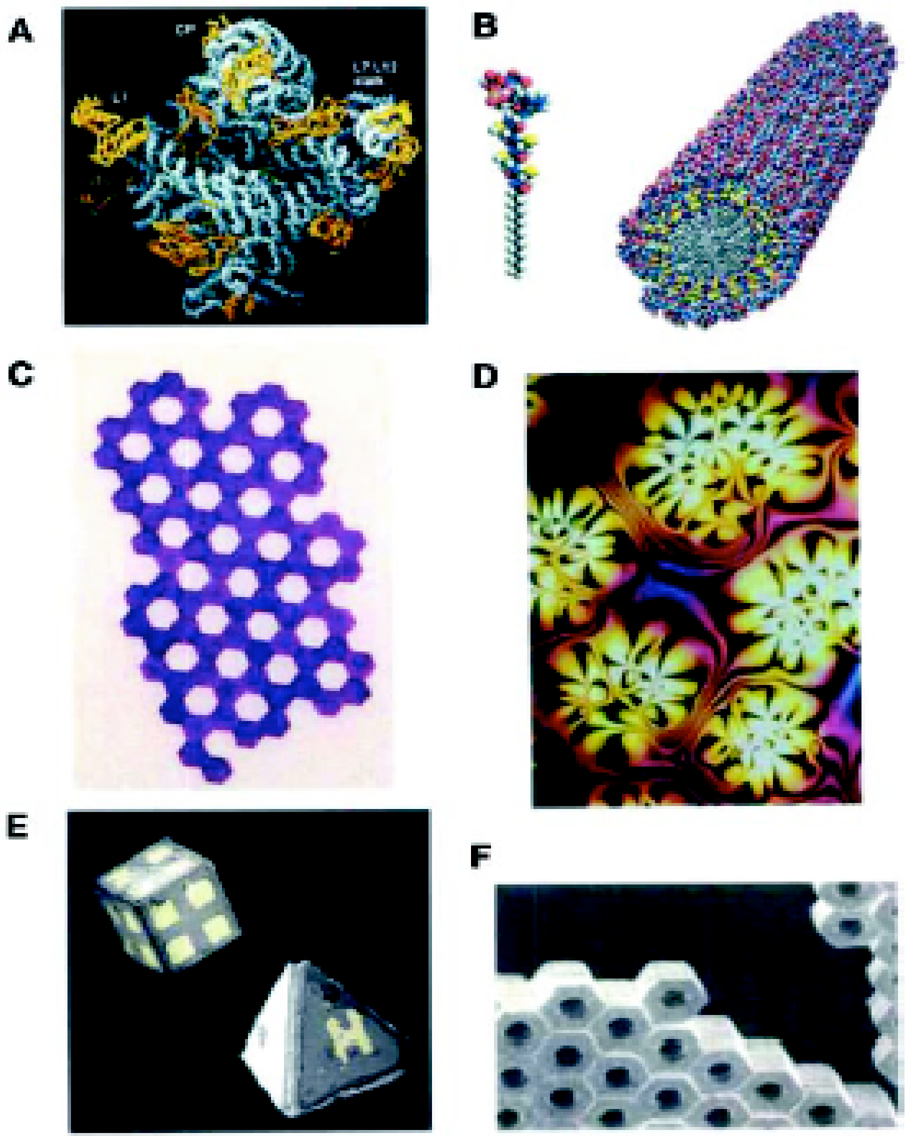


Table 1. Examples of self-assembly (S, static, D, dynamic, T, templated, B, biological).

Motivation

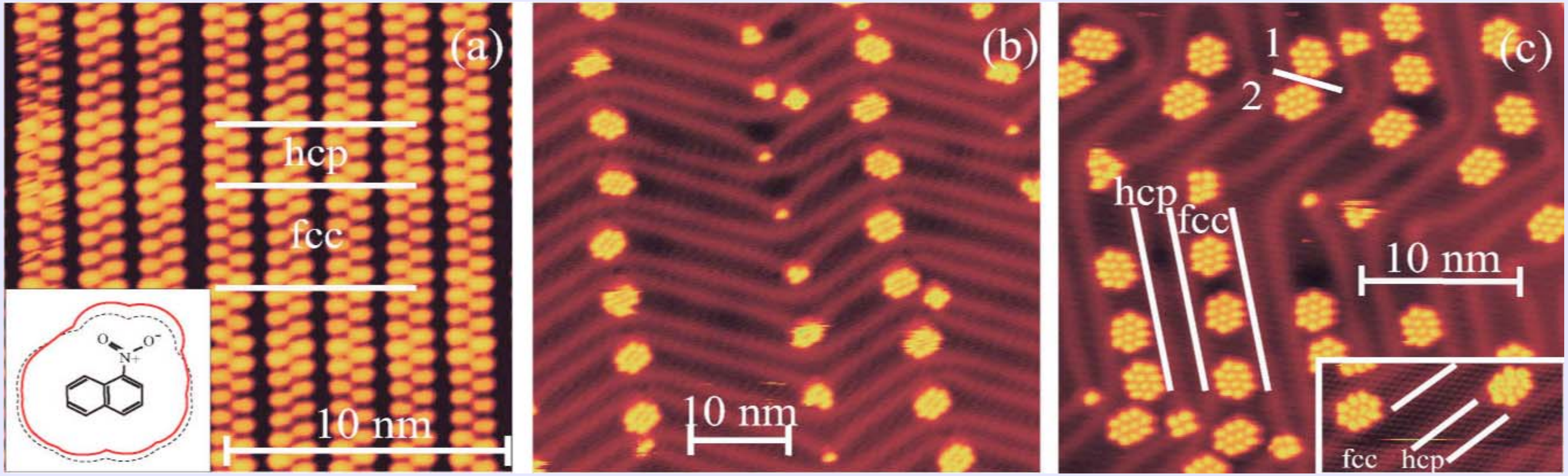
2 Dimensions:

- self-assembly of supramolecular structures :

  Direct electrostatic interaction between adsorbed molecules

Two-dimensional self-assembly of supramolecular chains & clusters

(1-Nitronaphthalene on Au(111))



M. Böhringer, K. Morgenstern, WDS, R. Berndt,
F. Mauri, A. De Vita, R. Car, PRL **83**, 324 (1999)

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Motivation

2 Dimensions:

- self-assembly of supramolecular structures :

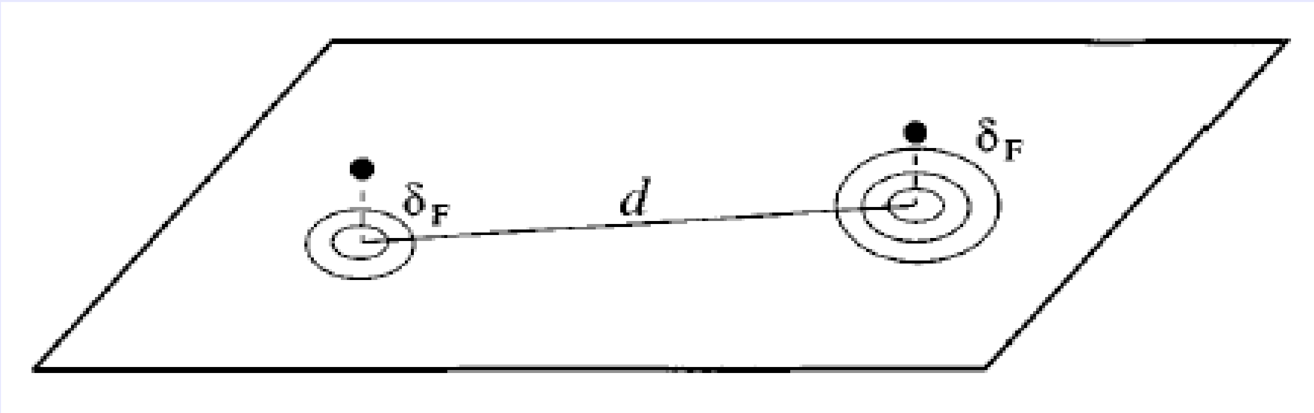
  Direct electrostatic interaction between adsorbed molecules

- self-assembly of an atomic superlattice?

  Substrate-mediated interaction with a 2 D electron gas

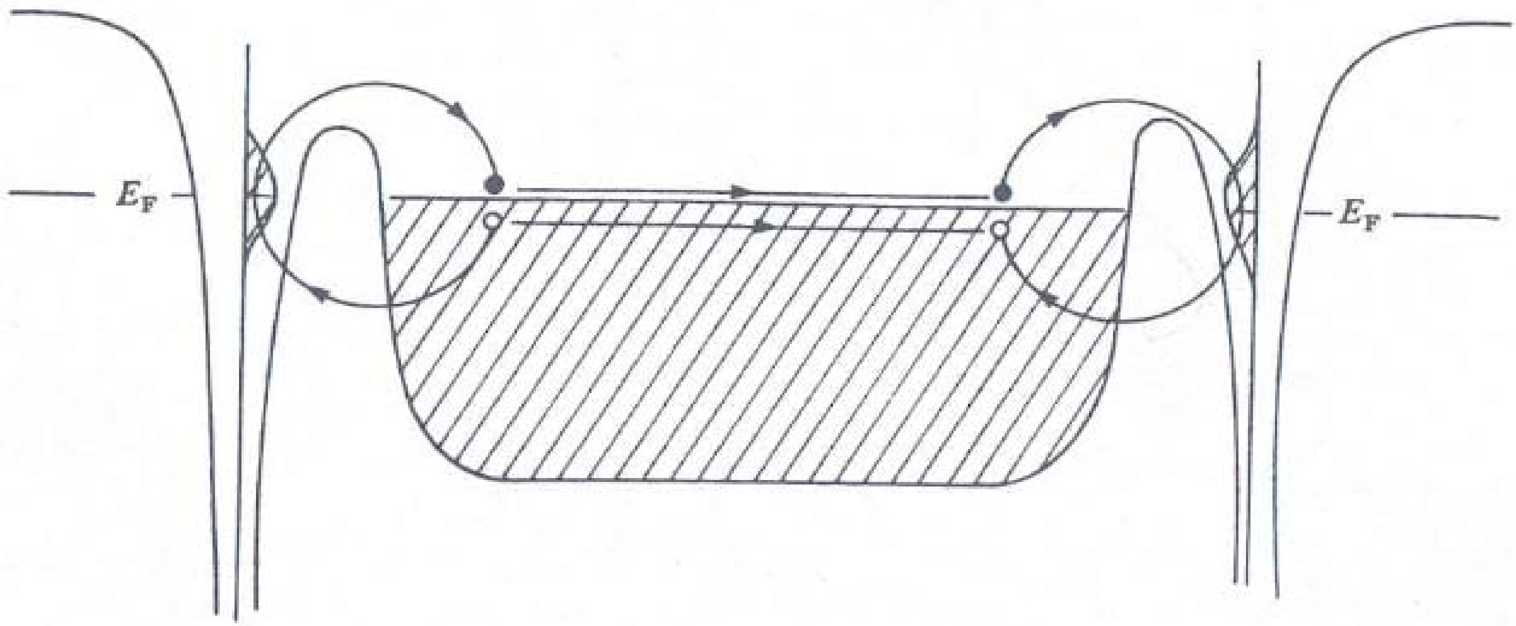
Indirect long-range oscillatory interactions between adsorbed atoms

K. H. Lau and W. Kohn, Surf. Sci. **75**, 69 (1978)



$\Delta E_{int} \sim \cos(2k_F d + \delta_F)/d^n$ $n = 2$ (surface)

Fig. 11.18. Schematic view of the indirect electronic interaction between two adsorbates in the resonant level model.



A. Zangwill, Physics at Surfaces

Long-range interaction between adatoms mediated by substrate electrons

Theory:

T. B. Grimley, Proc. Phys. Soc. 90, 751 (1967).

T. L. Einstein and J. R. Schrieffer, Phys. Rev. B 7, 3629 (1973).

➢ K. H. Lau and W. Kohn, Surf. Sci. 75, 69 (1978).

➢ P. Hyldgaard and M. Persson, J. Phys.: Condens. Matter 12, L13 (2000).

Experiments:

FIM

➢ T. T. Tsong, Phys. Rev. Lett. 31, 1207 (1973).

➢ F. Watanabe and G. Ehrlich, Phys. Rev. Lett. 62, 1146 (1989).

STM

M. N. Kamna, S. J. Stranick, and P. S. Weiss, Science 274, 119 (1996).

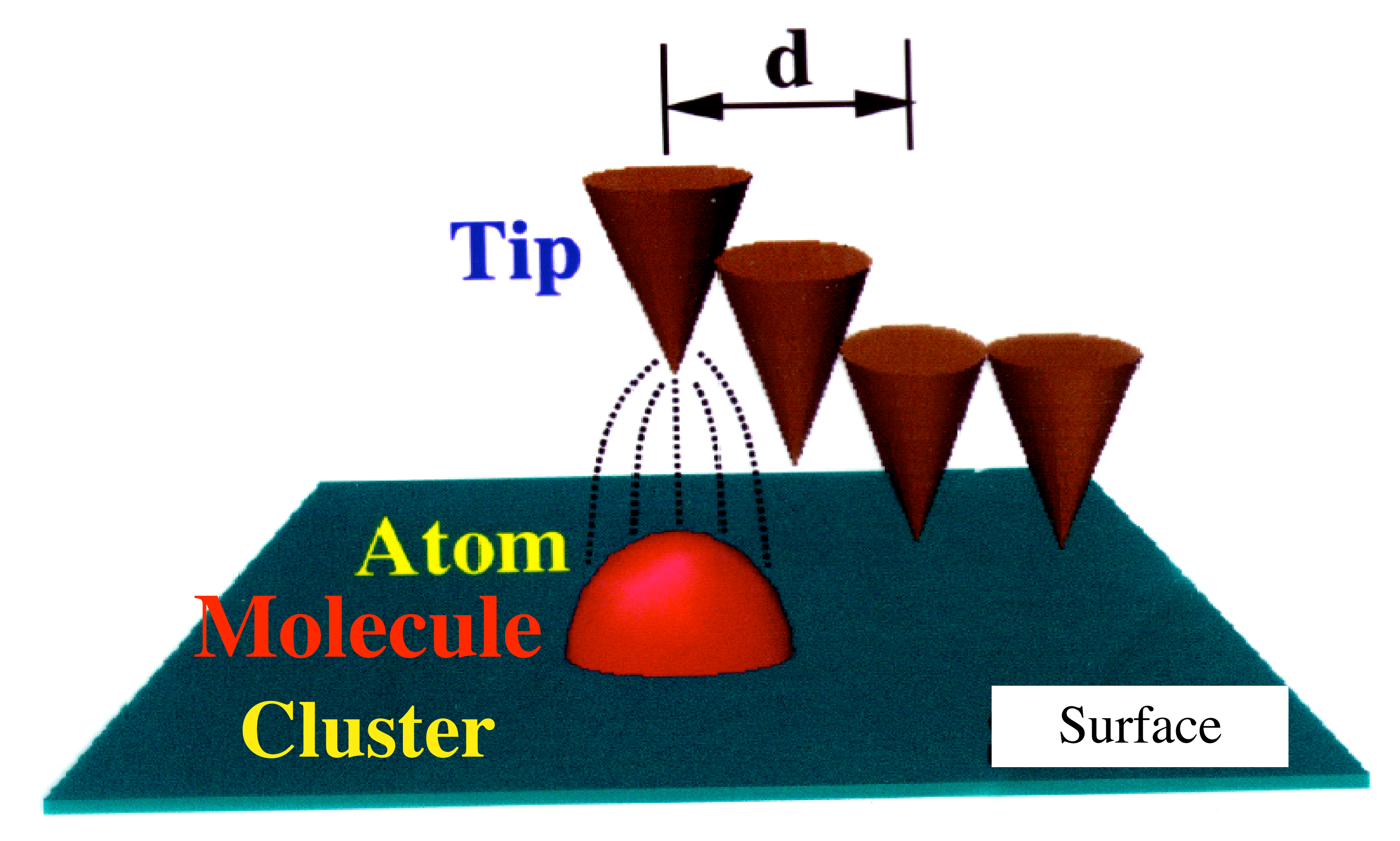
E. Wahlström, I. Ekvall, H. Olin, and L. Walldén, Appl. Phys. A: Mater. Sci. Process. A66, S1107 (1998).

➢ J. Repp, F. Moresco, G. Meyer, K. H. Rieder, P. Hyldgaard, and M. Persson, Phys. Rev. Lett. 85, 2981 (2000).

➢ N. Knorr, H. Brune, M. Epple, A. Hirstein, M. A. Schneider, and K. Kern, Phys. Rev. B 65, 115420 (2002).

But: No self-organisation of an adatom superlattice!

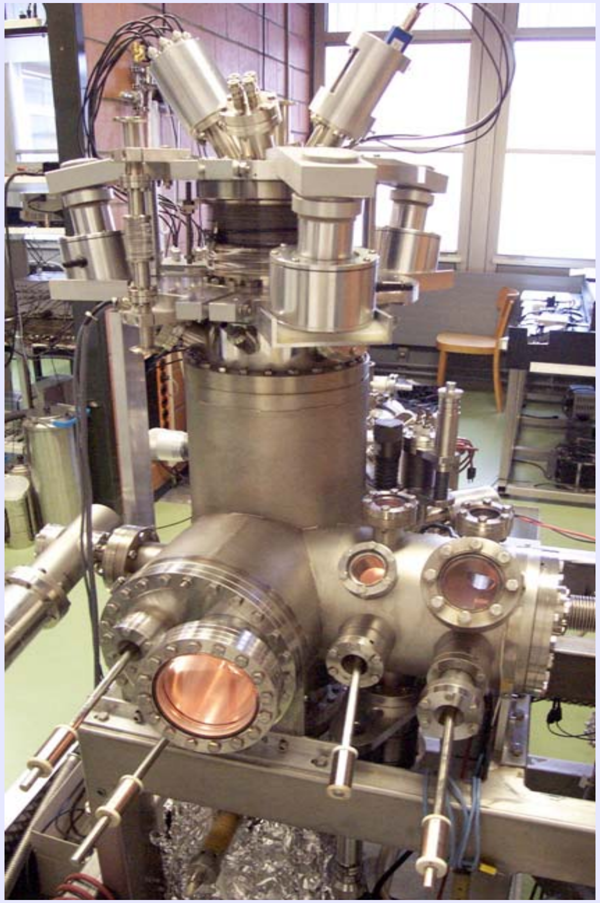
A typical « local » experiment at low temperature in UHV



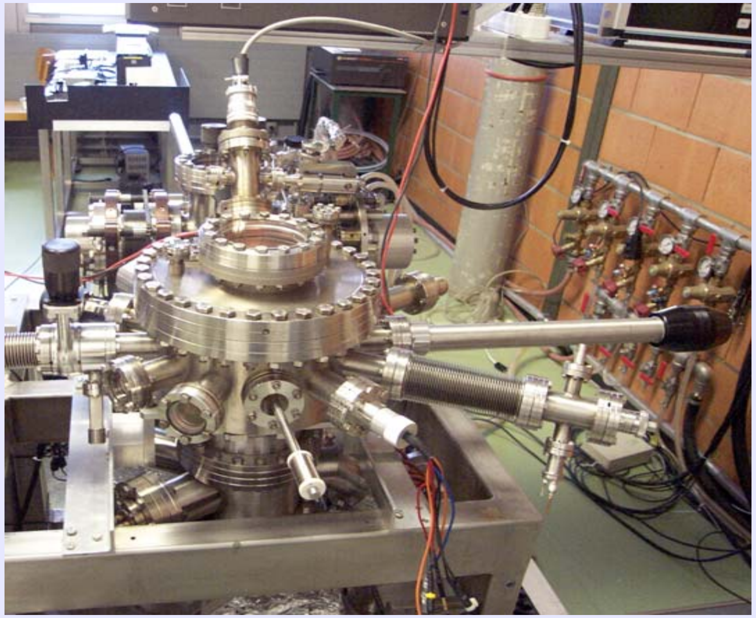
J. Li, PhD Thesis, Lausanne (1997)

Low-temperature STM
(50 K, 4.8 K, 3.9 K)

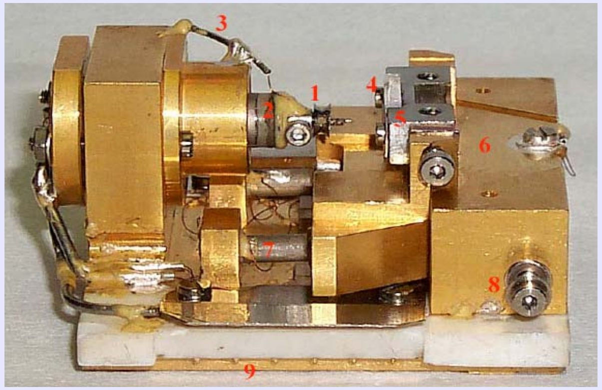
STM chamber



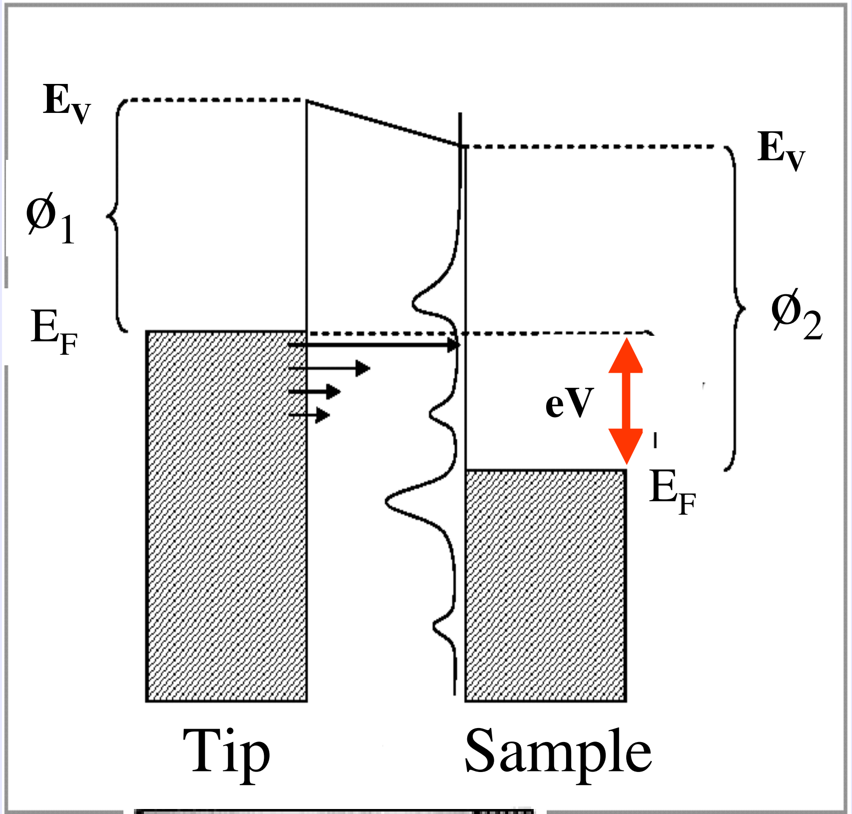
Preparation chamber

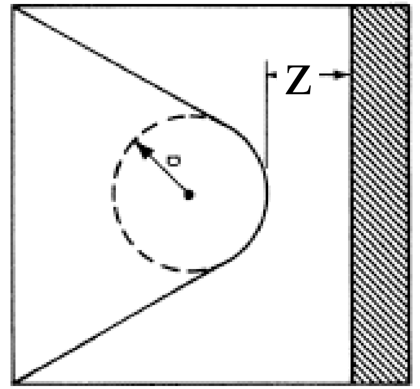


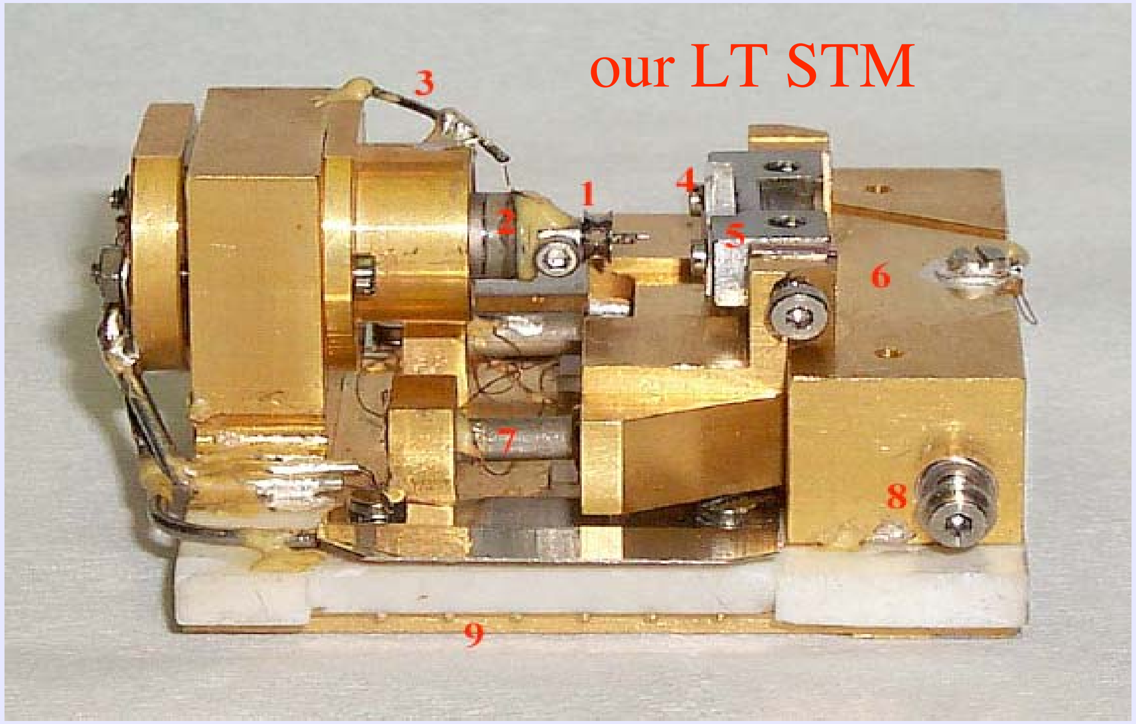
STM head



Scanning probe methods: STM, STS







$$I(V) \propto \int_0^{eV} \rho_t(\pm eV \mp E)\, \rho_s(E)\, T(E, eV)\, dE$$

$$\frac{dI}{dV}(V) \propto e\, \rho_t(0)\, \rho_s(eV)\, T(eV, eV)$$

Electrons in surface states: Scattering and confinement on noble metal (111) surfaces

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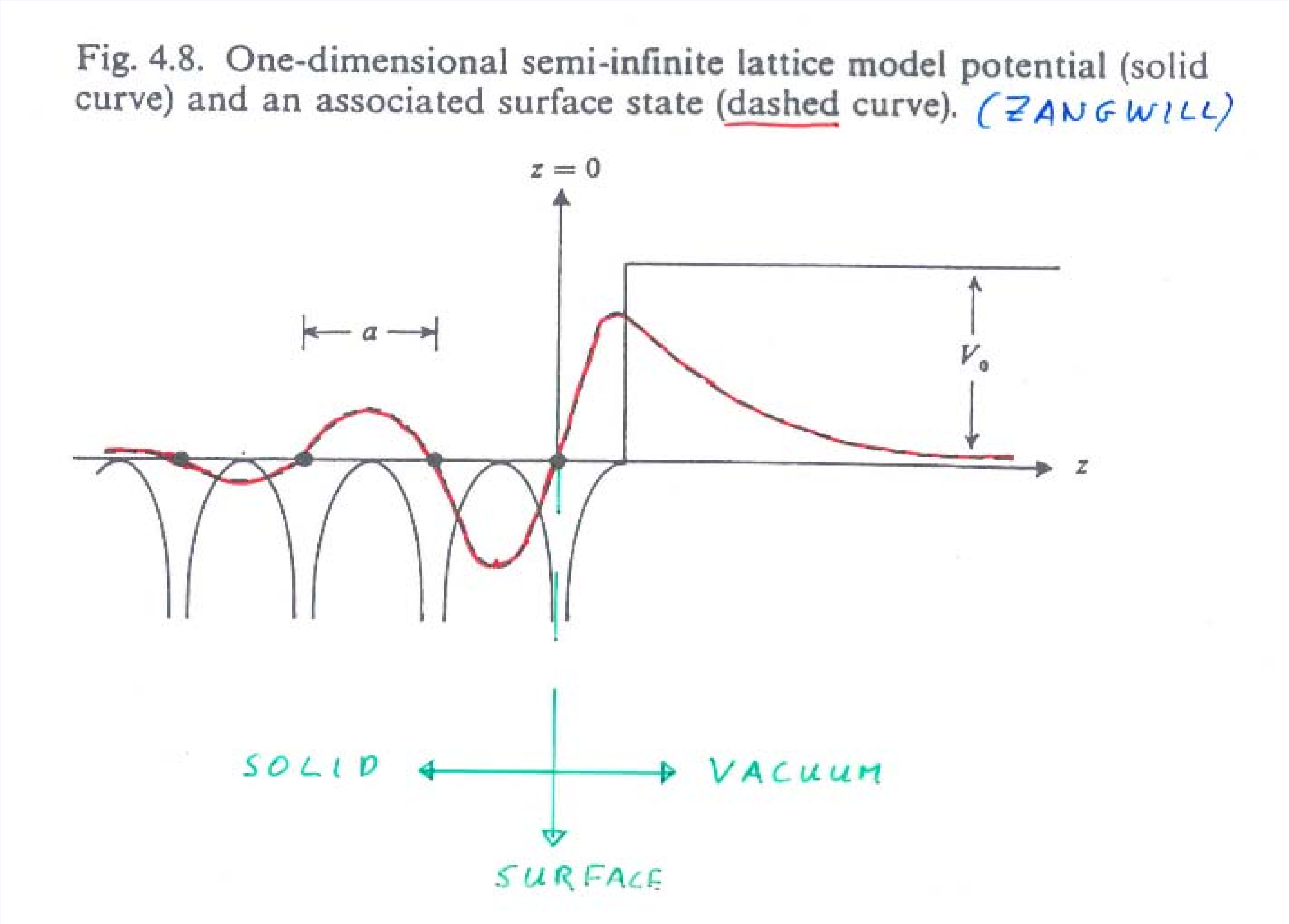
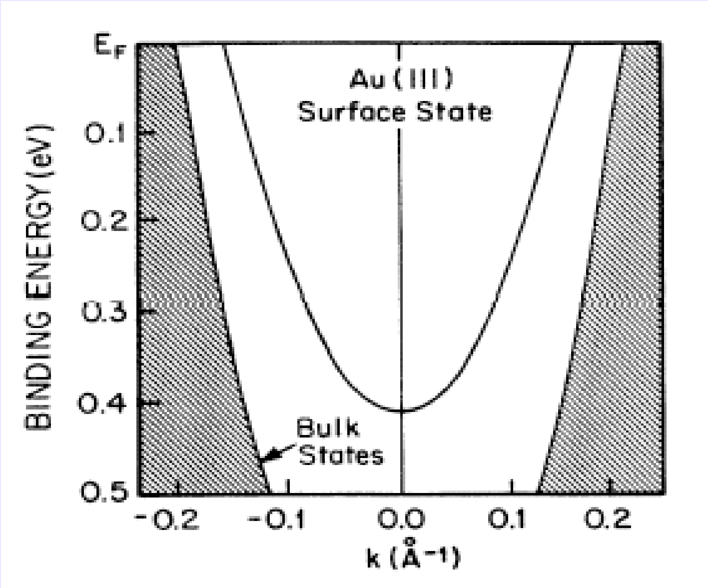
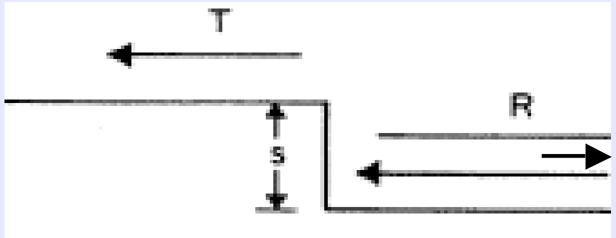


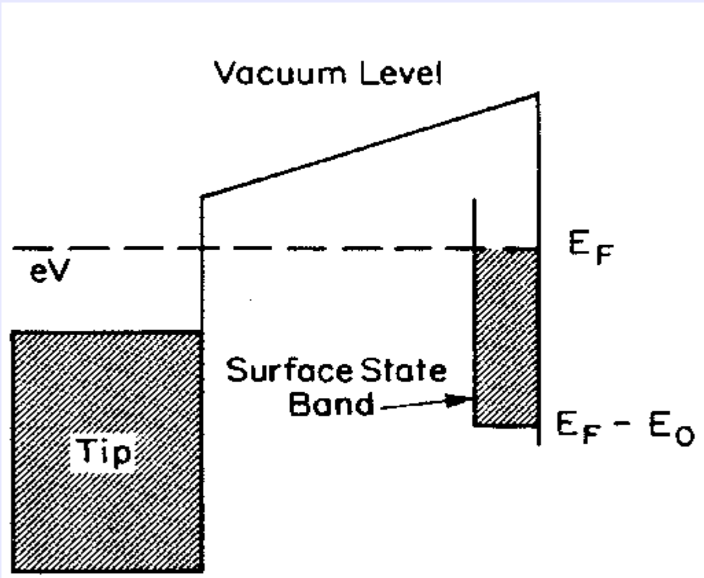
A. Zangwill, Physics at Surfaces

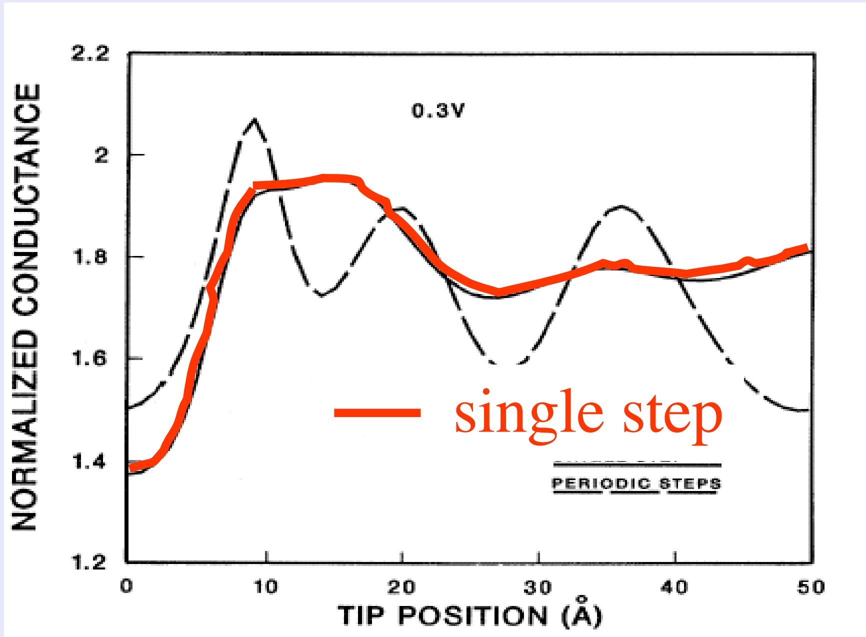
Electrons in a surface state





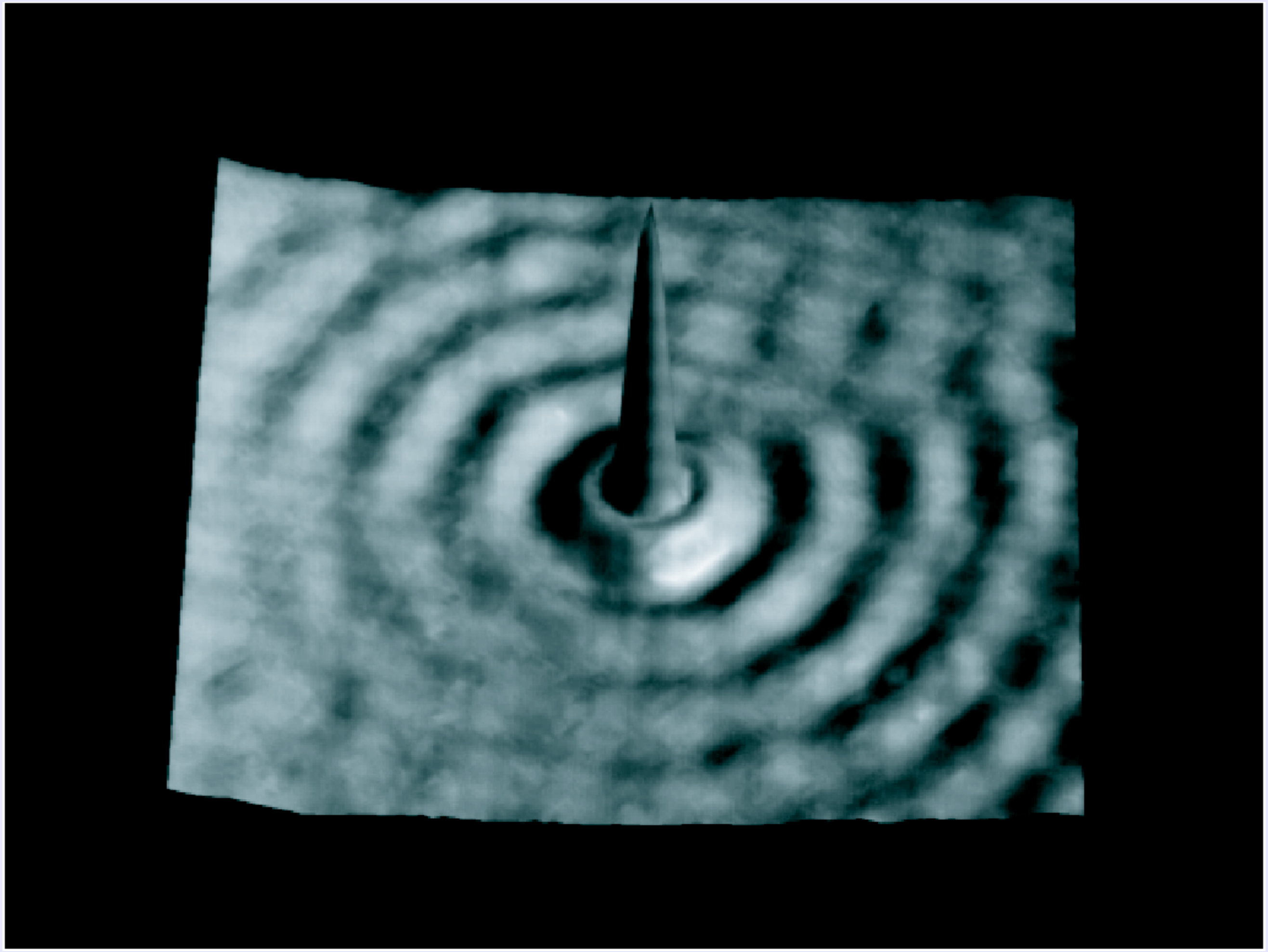
$$\psi(x)=\begin{cases} e^{-iqx}+Re^{iqx}, & x>0 \\ Te^{-iqx}, & x<0 \end{cases}$$





L. C. Davis et al., PRB **43**, 3821 (1991)

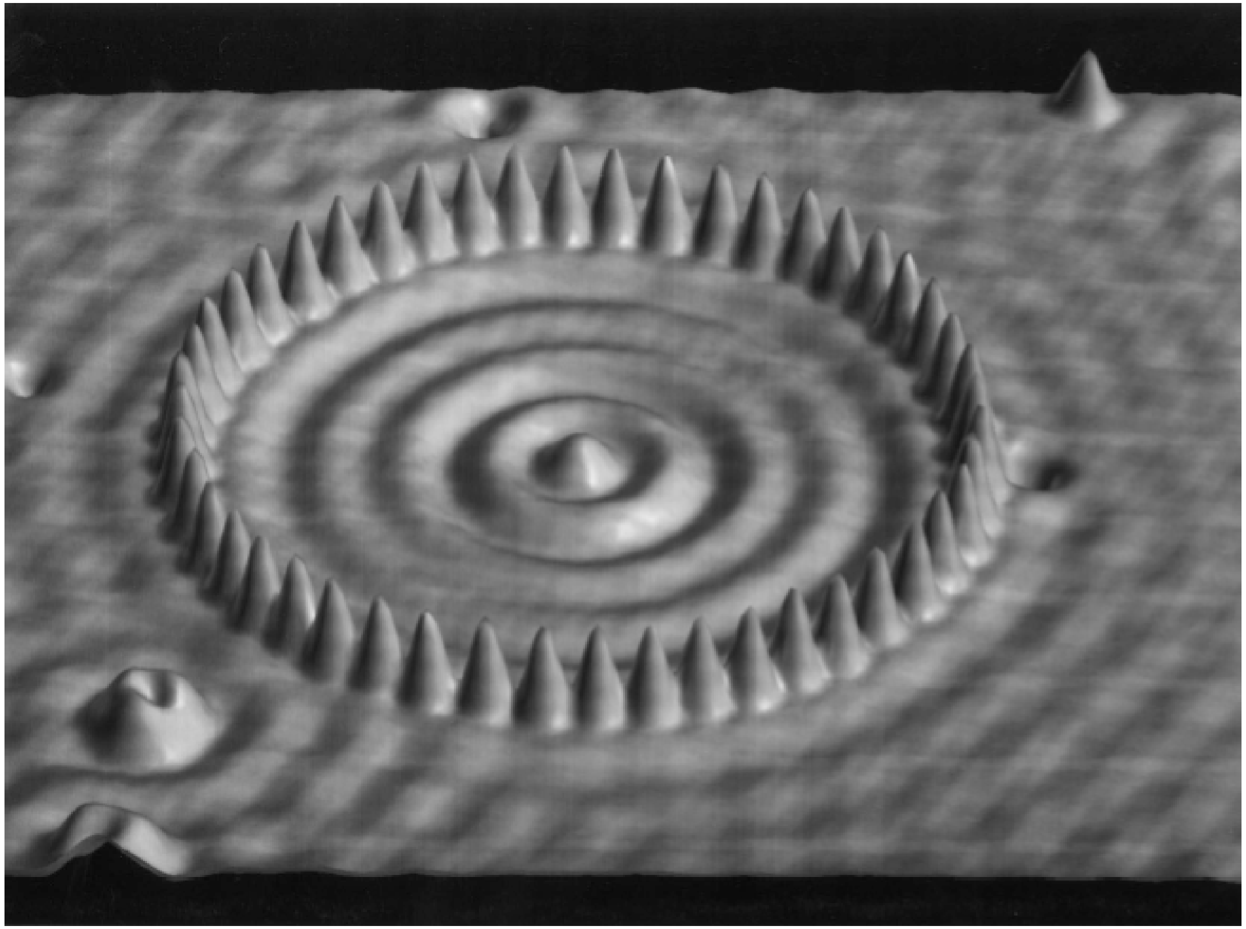
Electron standing waves: Fe atom on Cu(111)



13 nm^2,
Fe/Cu(111)

M. F. Crommie, C. P. Lutz, D. M. Eigler, Science **262**, 218 (1993)

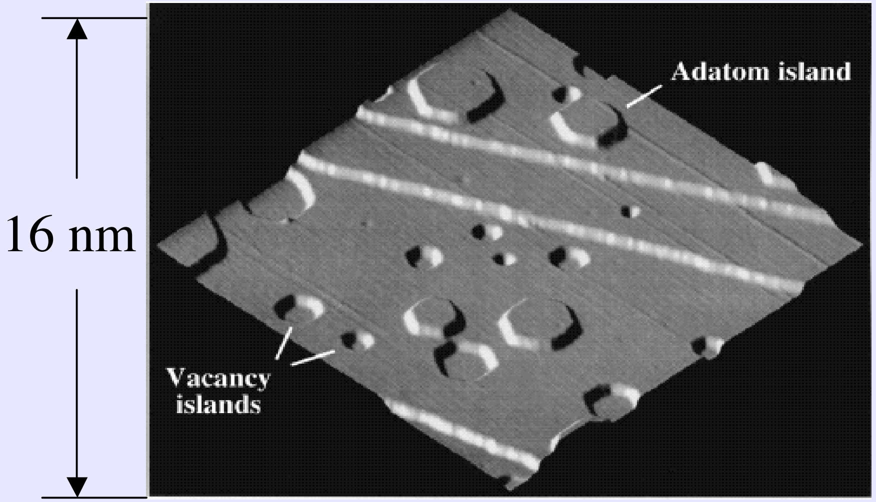
Electron standing waves in a quantum corral



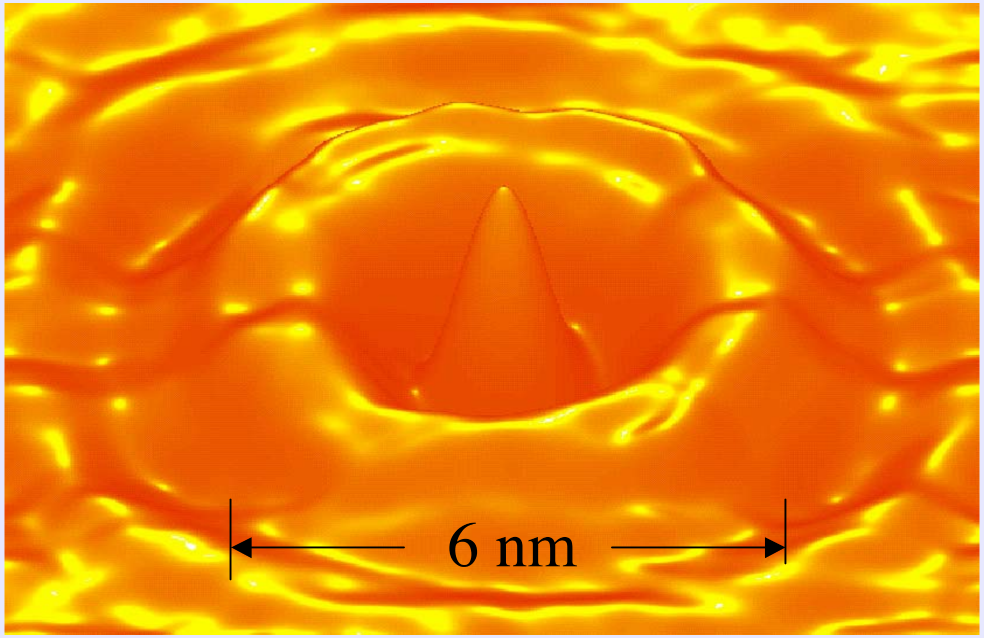
48 Fe atoms on Cu(111)

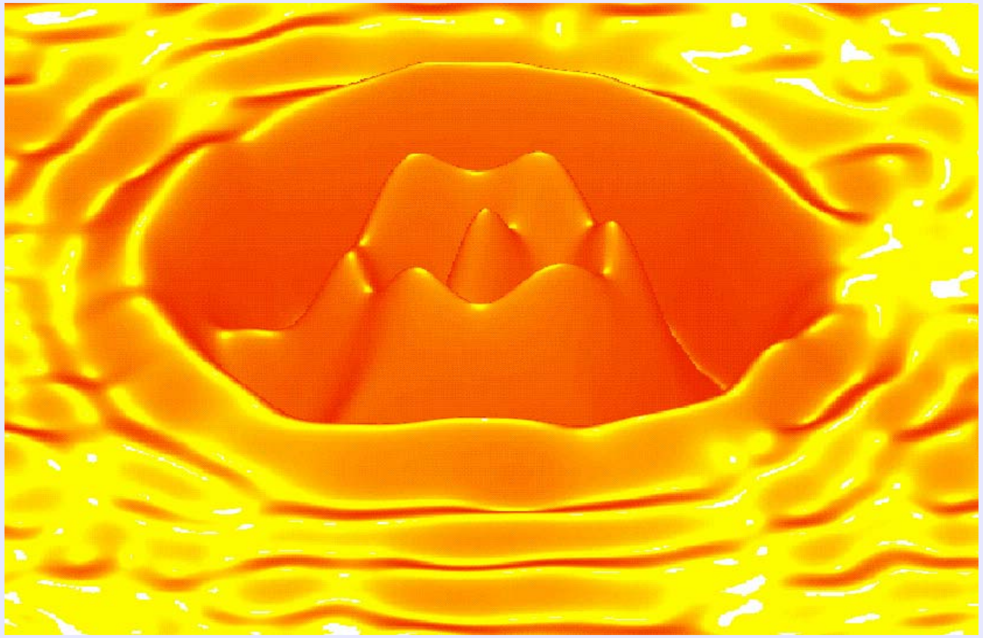
Ø = 14.26 nm

M. F. Crommie, C. P. Lutz, D. M. Eigler, Science **262**, 218 (1993)



Electron confinement to nanoscale Ag islands: Ag(111)

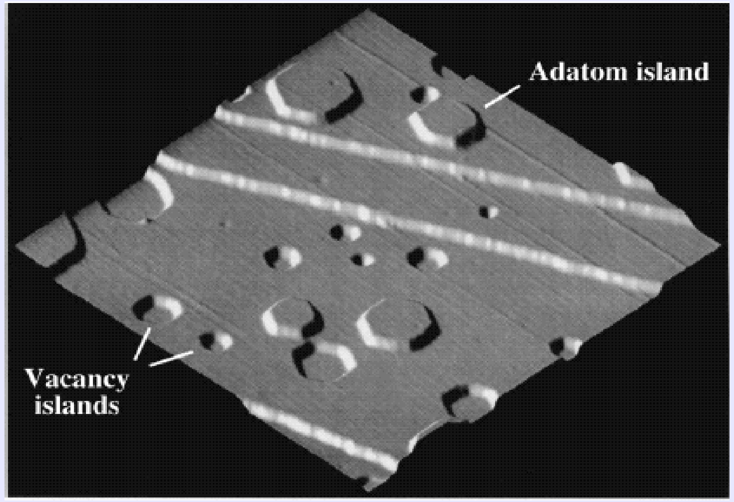


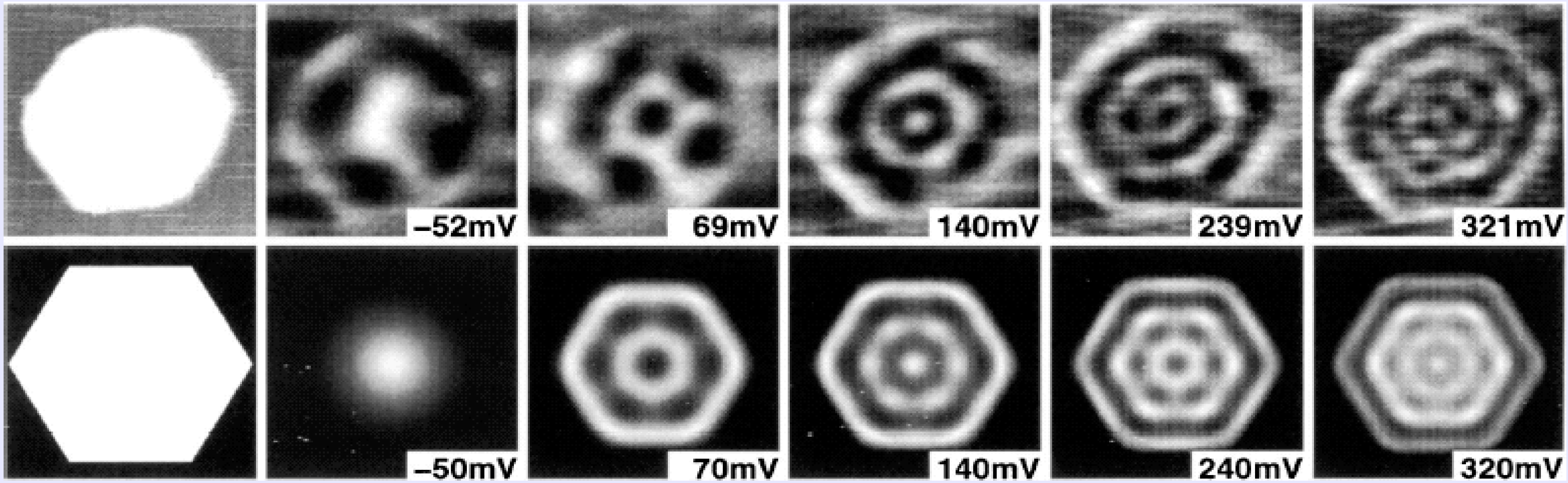


J. Li, PhD thesis, University of Lausanne (1997)

Electron confinement to Ag islands on Ag(111)

16 nm





6 nm

J. Li, WDS, R. Berndt, S. Crampin, PRL **80**, 3332 (1998)

Quantum well states on a Ag(111) terrace

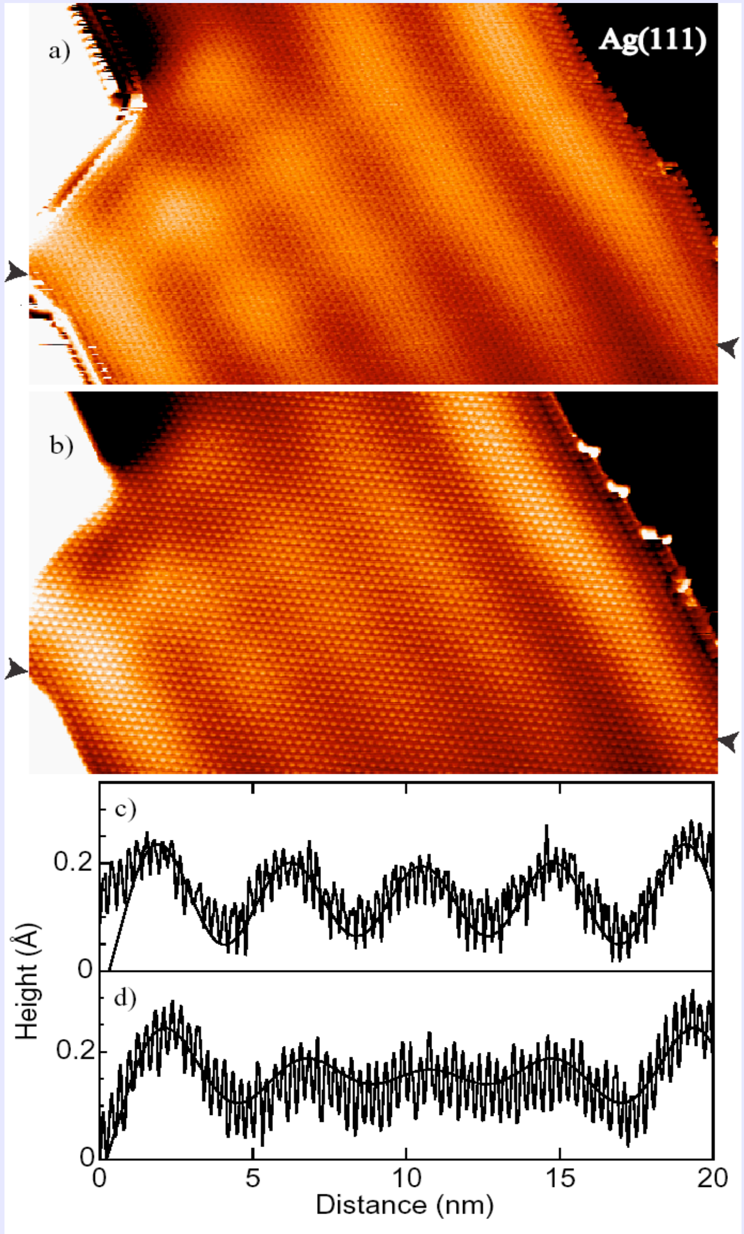
$$LDOS(E, x) \propto \sum_n \frac{|\psi_n(x)|^2}{\sqrt{E - E_n}}; \qquad n| \quad E_n \le E.$$

For an ideal tip (point probe):

J. Tersoff and D. R. Hamann, PRB 31, 805 (1985)

$$I(V, x) \propto \int_{E_F}^{eV} \sum_n \frac{|\psi_n(x)|^2}{\sqrt{E - E_n}} dE; \quad n| \quad E_n \le E$$

M. Pivetta, F. Silly, F. Patthey, J. P. Pelz, WDS, PRB **67**, 193402 (2003)



2D electron gas:

Scattering at adatoms

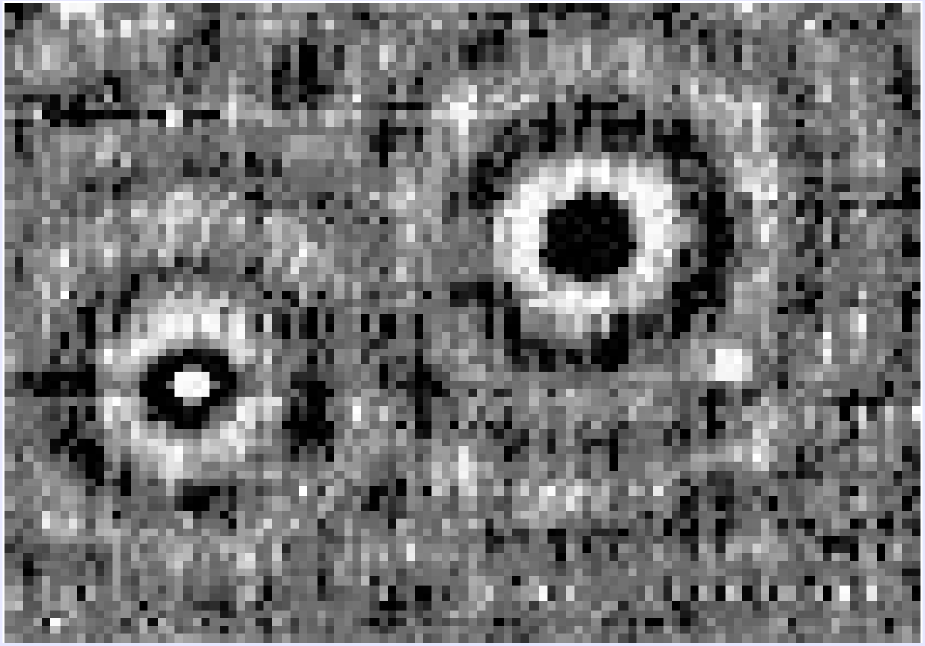
↓

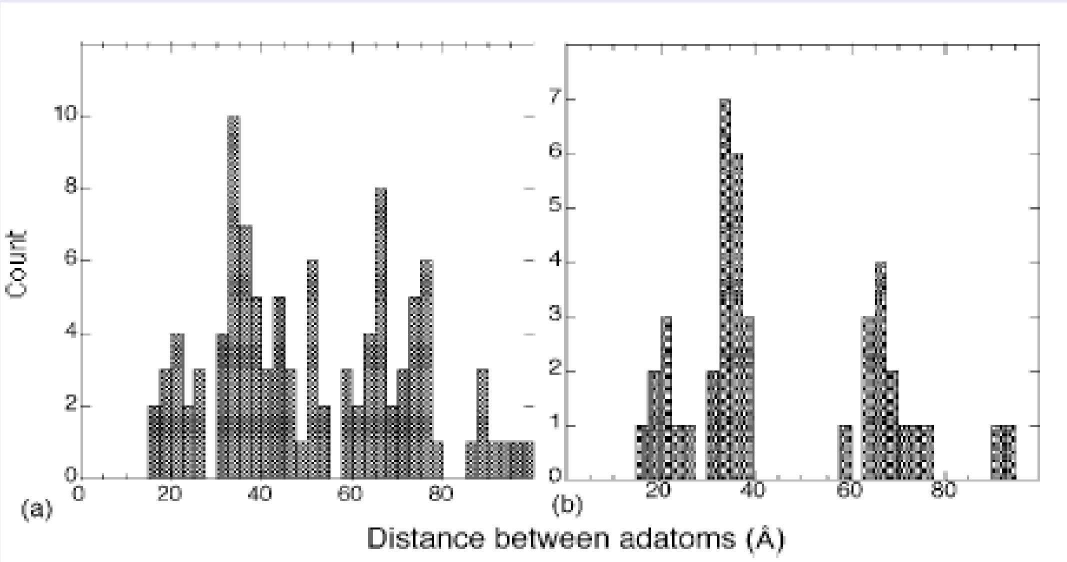
Standing waves

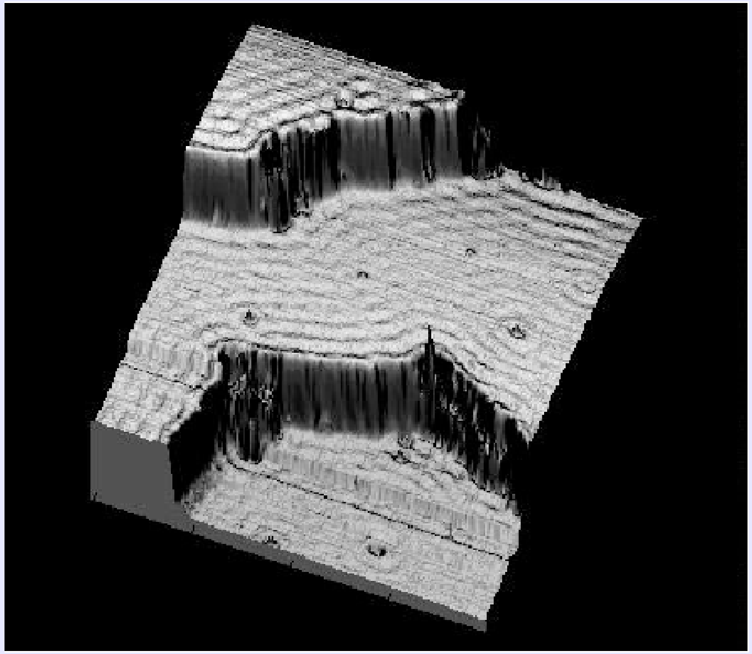
↓

Interaction between adatoms

S(?) on Cu(111)





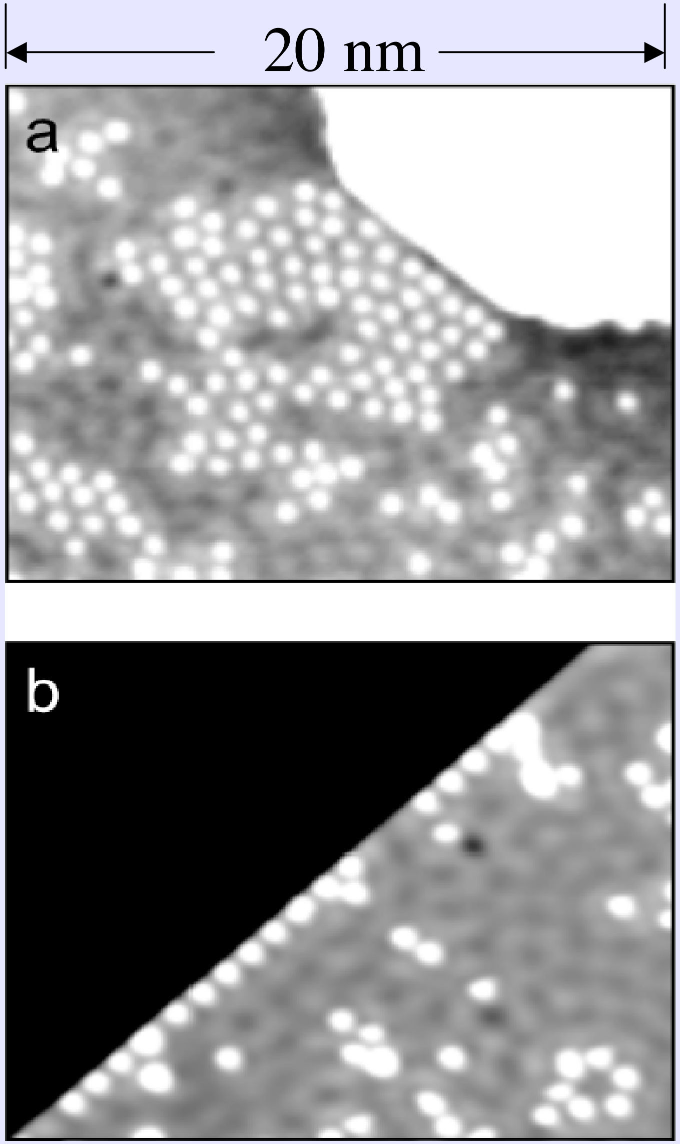


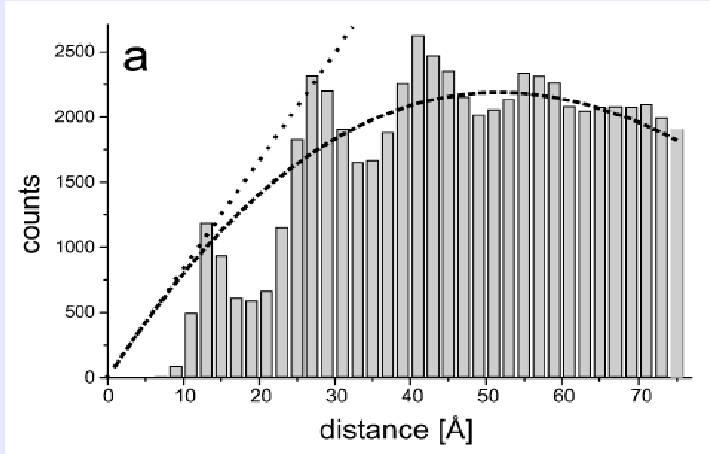
$$\Delta E_{int} \sim \cos(2k_F d + \delta_F)/d^n$$

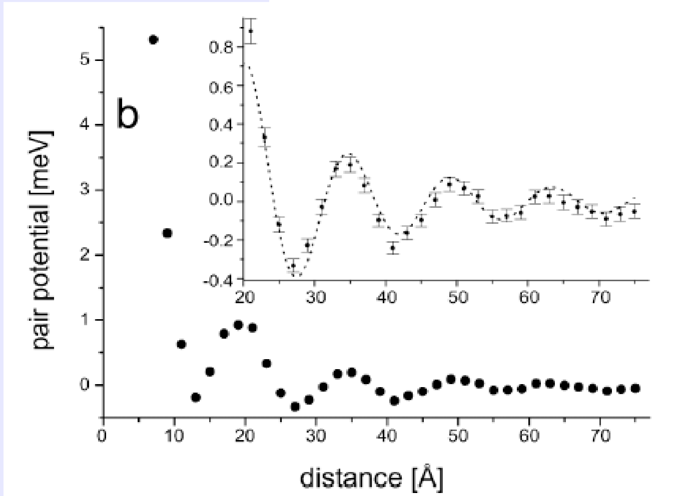
$$n = 2$$

E. Wahlström, I. Ekvall, H. Olin, L. Walldén, Appl. Phys. A **66**, S1110 (1998)

Cu on Cu(111)



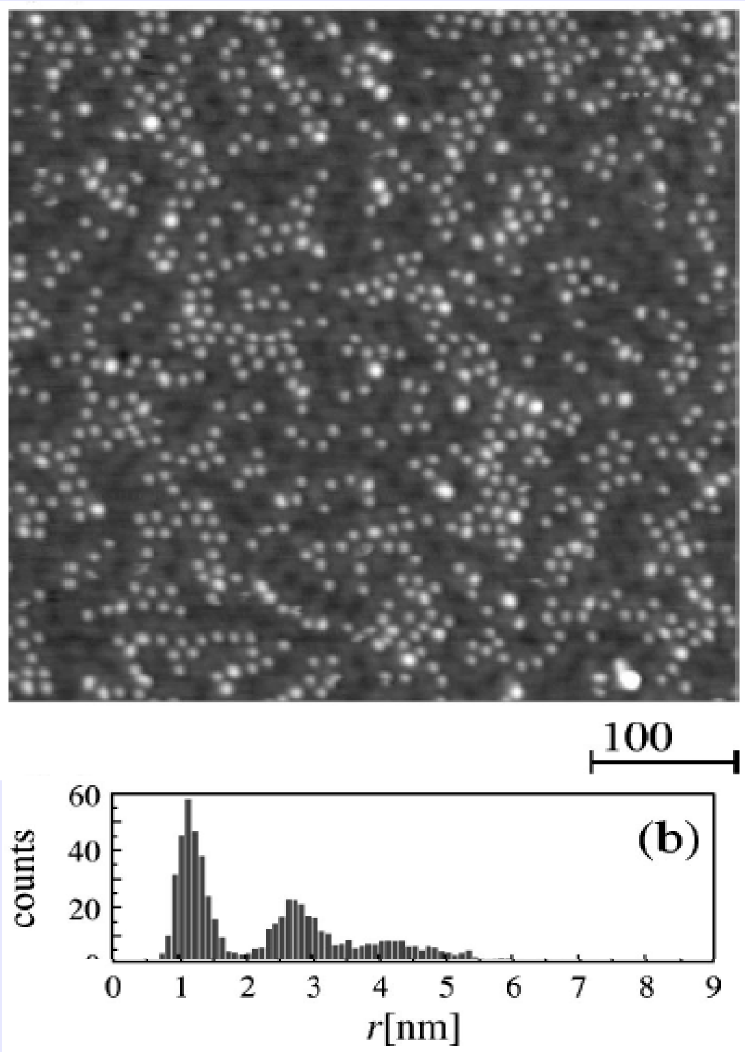




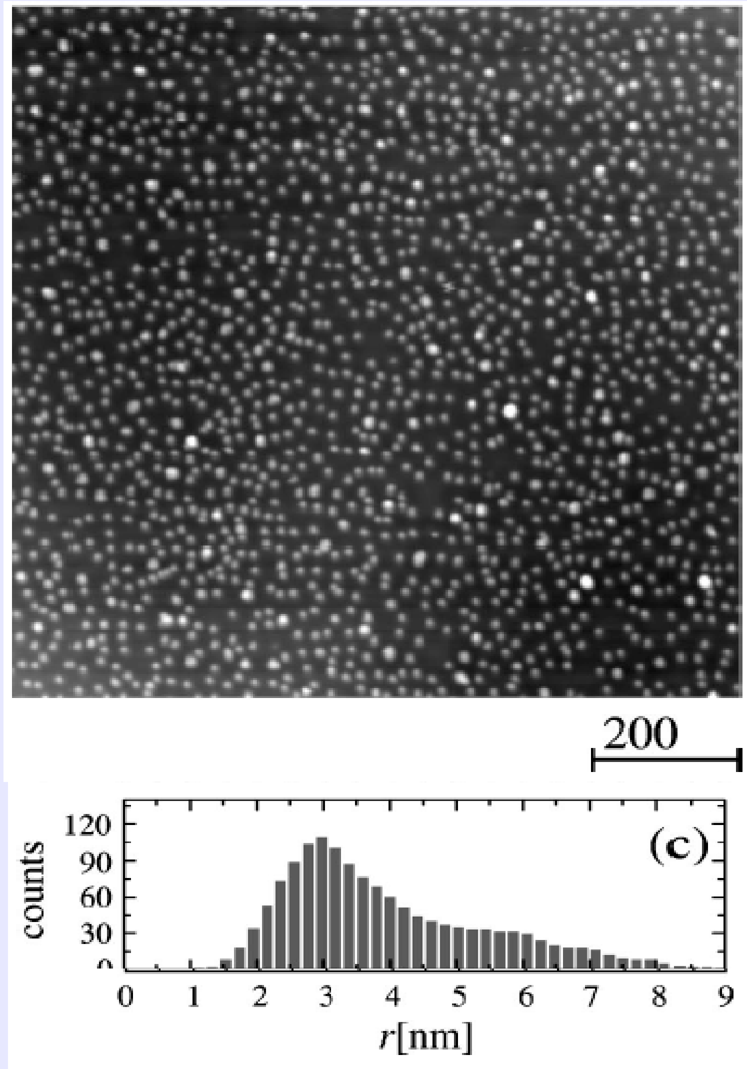
$$E(d) \simeq -A(\delta_F, r)\left(\frac{4\epsilon_F}{\pi^2}\right)\frac{\sin(2q_F d + 2\delta_F)}{(q_F d)^2}$$

J. Repp, F. Moresco, G. Meyer, K. H. Rieder, P. Hyldgaard, M. Persson, PRL **85**, 2981 (2000)

Co/Cu(111)



Co/Ag(111)



N. Knorr, H. Brune, M. Epple, A. Hirstein, M. A. Schneider, K. Kern, PRB **65**, 115420 (2002)

Creation of an atomic superlattice by immersing metallic adatoms in a two-dimensional electron sea

F. Silly, M. Pivetta, M. Ternes, F. Patthey, J. P. Pelz, WDS, PRL **92**, 016101 (2004)

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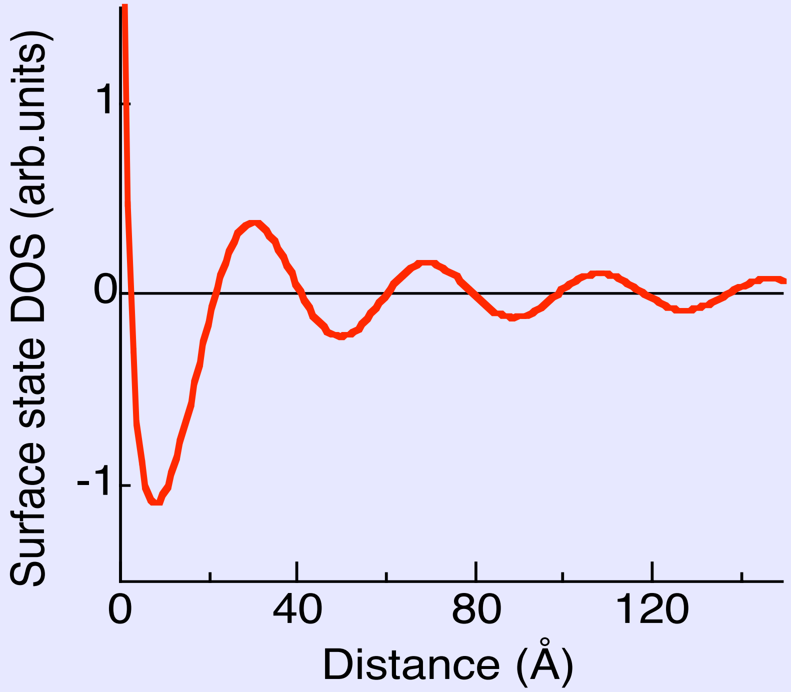
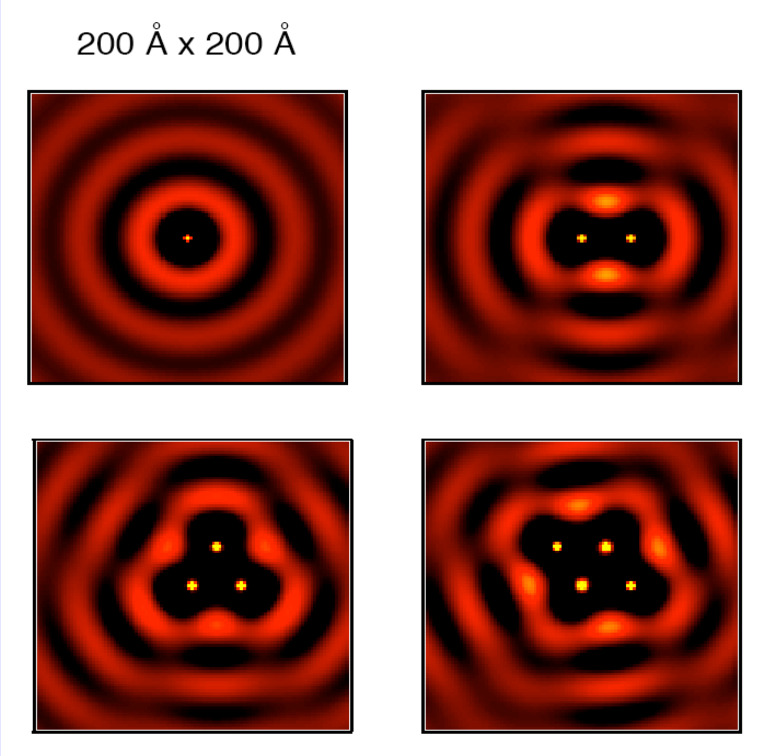
Simulation of the surface state LDOS oscillation at E_F : "Construction" of a superlattice

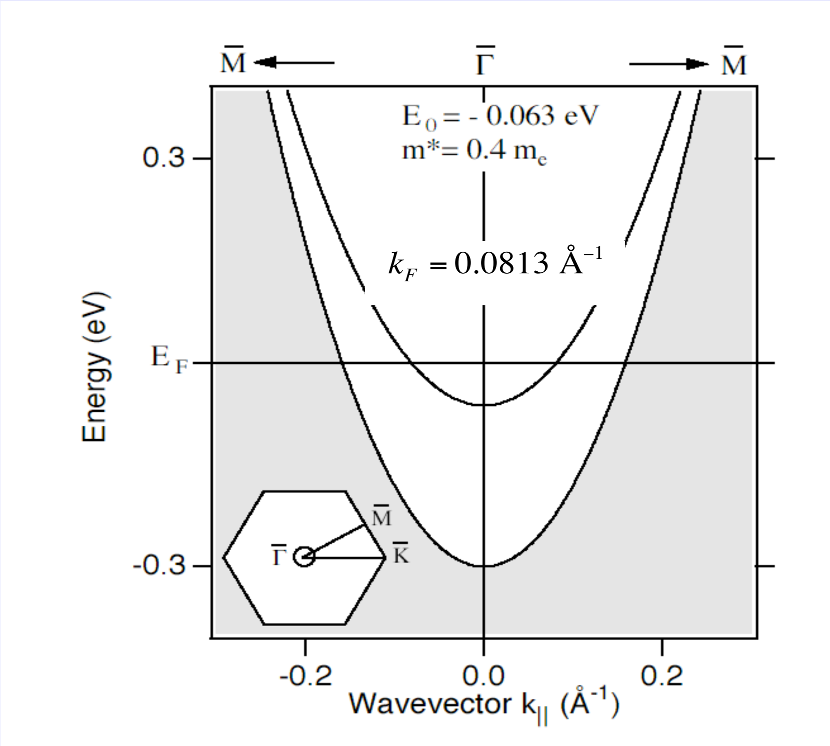




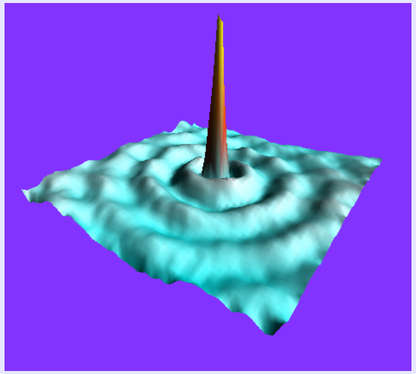
$$\Delta D(r) \propto \frac{1}{k_F r}\left(\cos^2(k_F r - \frac{\pi}{4} + \delta_0) - \cos^2(k_F r - \frac{\pi}{4})\right)$$

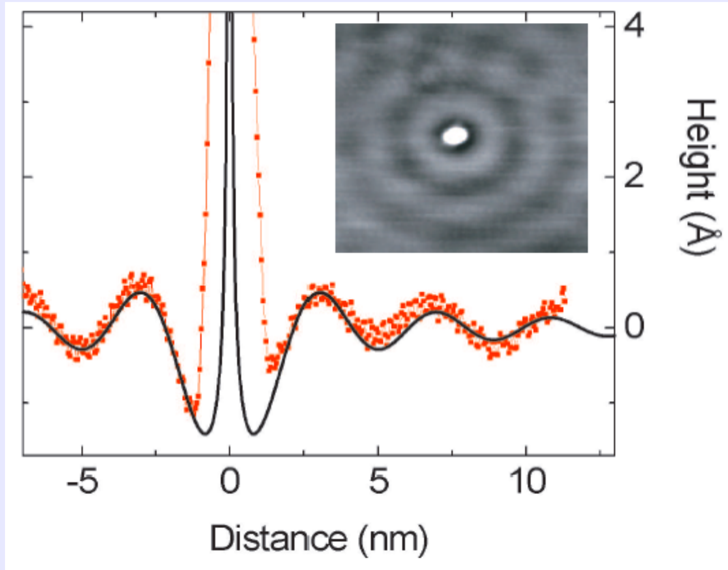
M. F. Crommie, C. P. Lutz, and D. M. Eigler
Nature 363, 524 (1993).

Determination of the phase shift at E_F for Ce on Ag(111)



210 Å x 210 Å
V = -3 mV, I = 19 pA
T = 3.9 K





$$\Delta D(r) \propto \frac{1}{k_F r}\left(\cos^2(k_F r - \frac{\pi}{4} + \delta_0) - \cos^2(k_F r - \frac{\pi}{4})\right)$$

$\Longrightarrow$

$\lambda_F = 2\pi / k_F$
$\lambda_F / 2 = 38$ Å

first maximum: 32 Å
$\delta_0 = (0.37 \pm 0.05)\pi$

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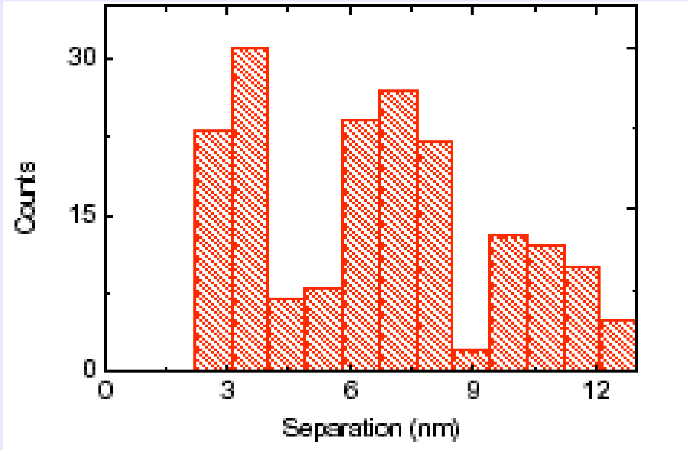
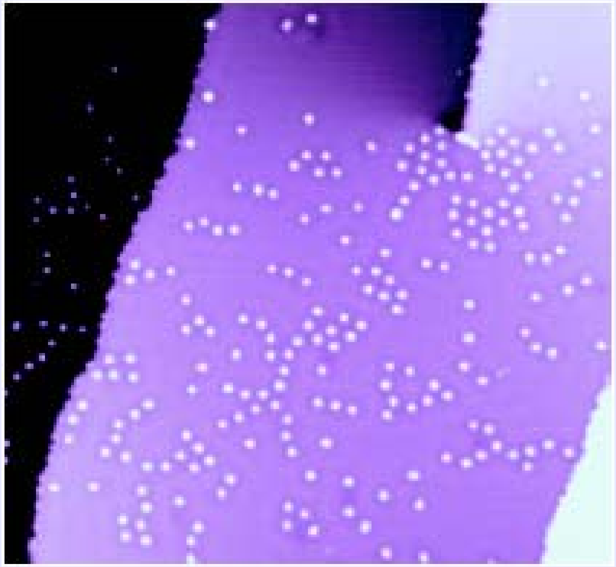
0.02 % of a ML Ce/Ag(111) @ 3.9 K

210 x 210 nm^2
U = -100 mV, I = 20 pA

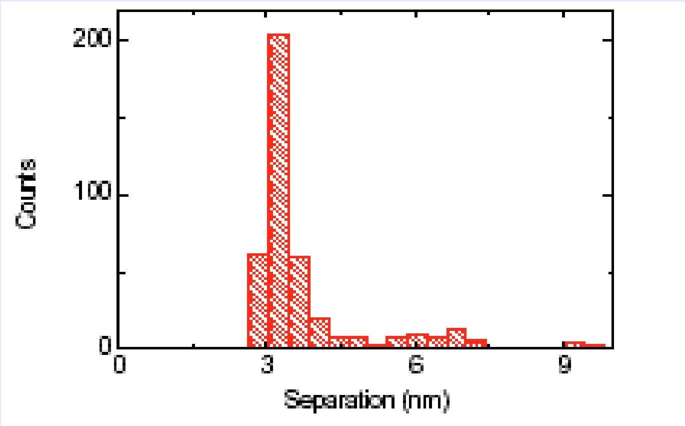


Histogram of
nearest neighbor - separations

0.2 % of a ML Ce/Ag(111) @ 3.9 K



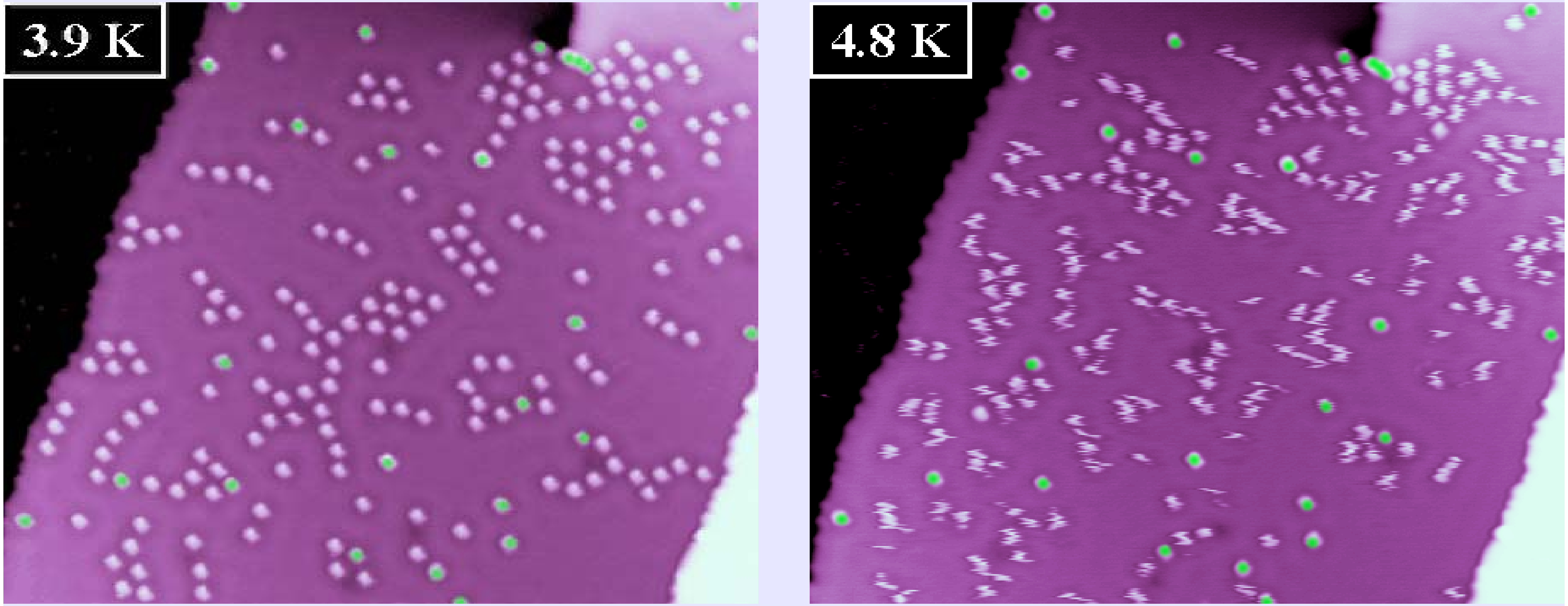
105 x 105 nm^2
U = -100 mV, I = 20 pA



Histogram of
nearest neighbor - separations

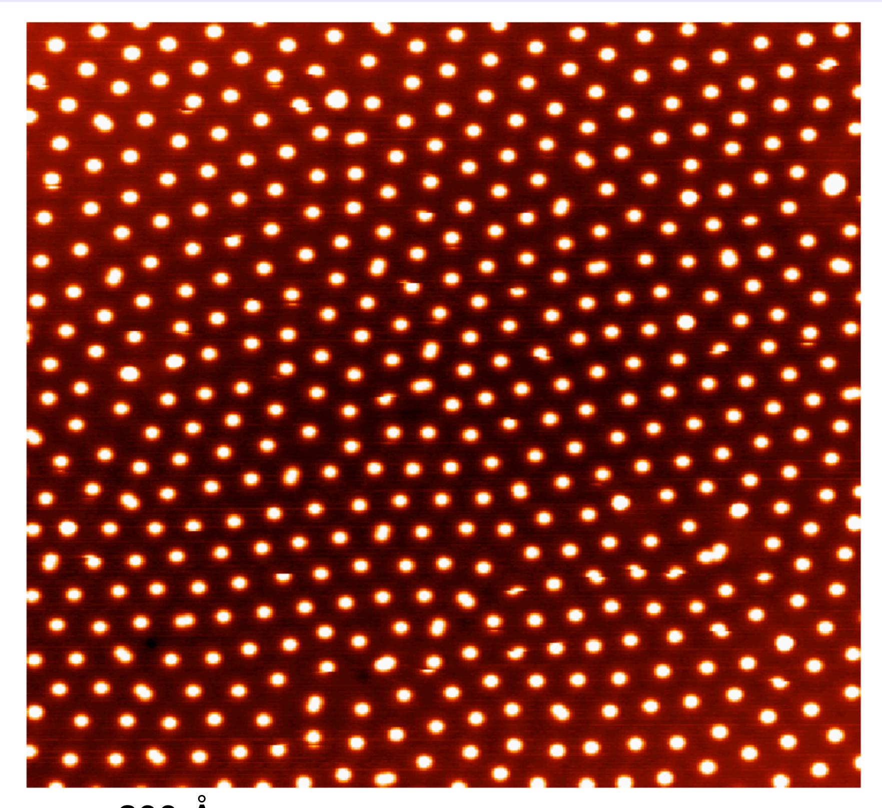
see also for Co/Cu(111): V. S. Stepanyuk et al., PRB, in print

Ce adatom mobility at low temperature and low concentration (≤ 0.1%ML)



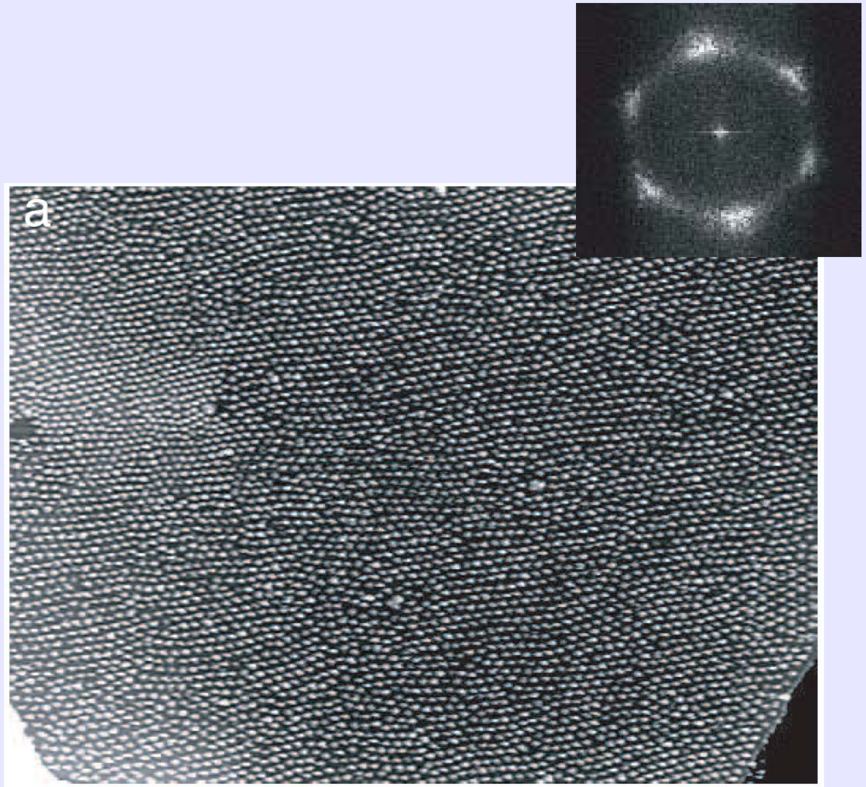
20 pA, -100 mV

1 % of a ML of Ce on Ag(111)



200 Å

630 Å x 630 Å
V = -100 mV, I = 20 pA
T = 3.9 K



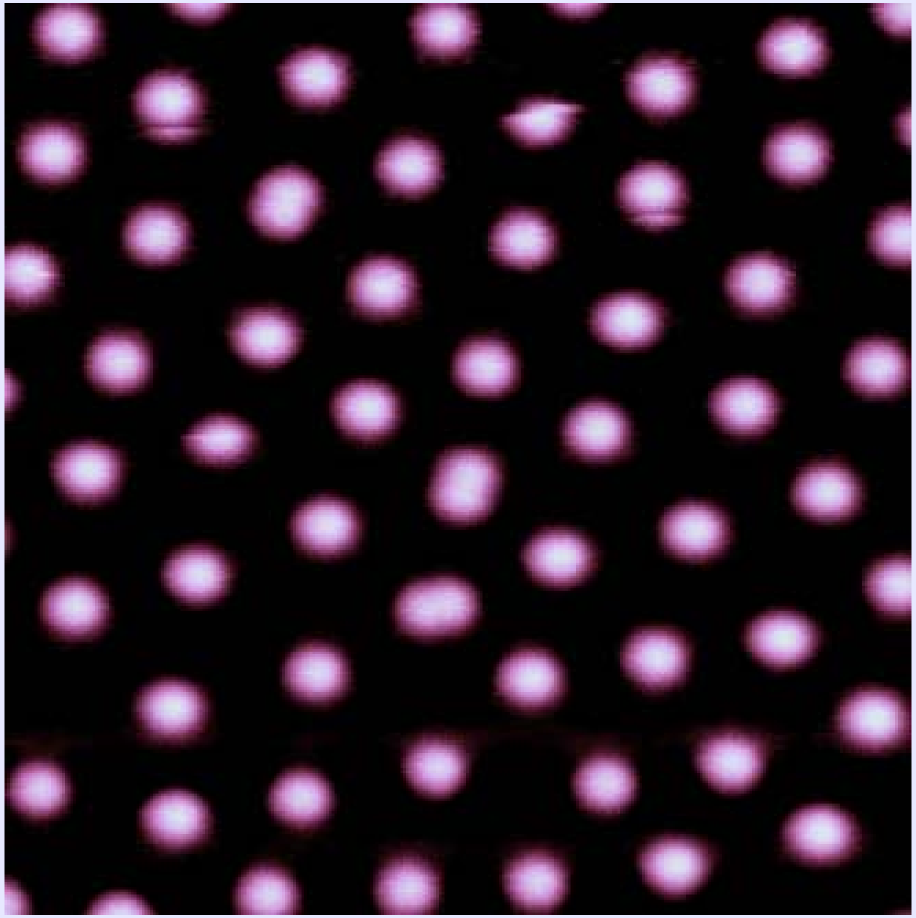
1000 Å

2400 Å x 1900 Å
V = -200 mV, I = 30 pA
T = 4.8 K

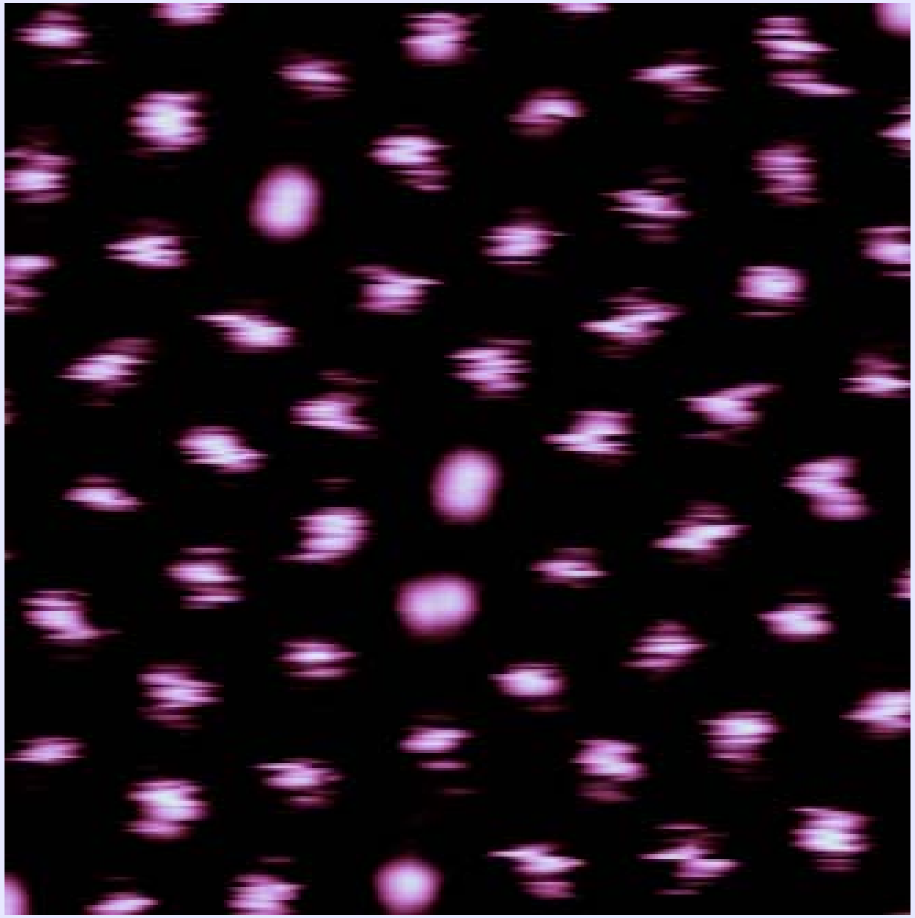
- 2D hexagonal superlattice of Ce adatoms
- Average nearest neighbor distance: 32 Å

Adatom hopping in the superlattice

T= 3.9 K Hopping time: 150s

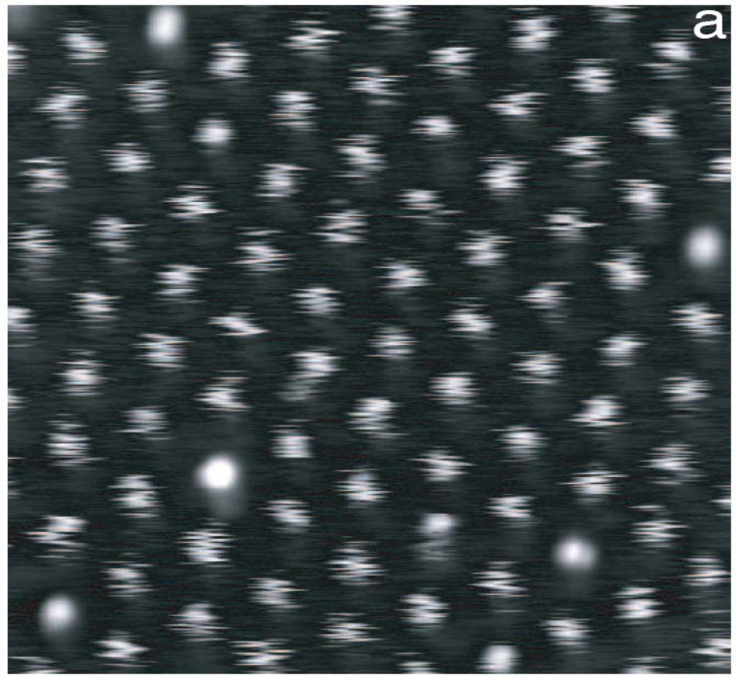


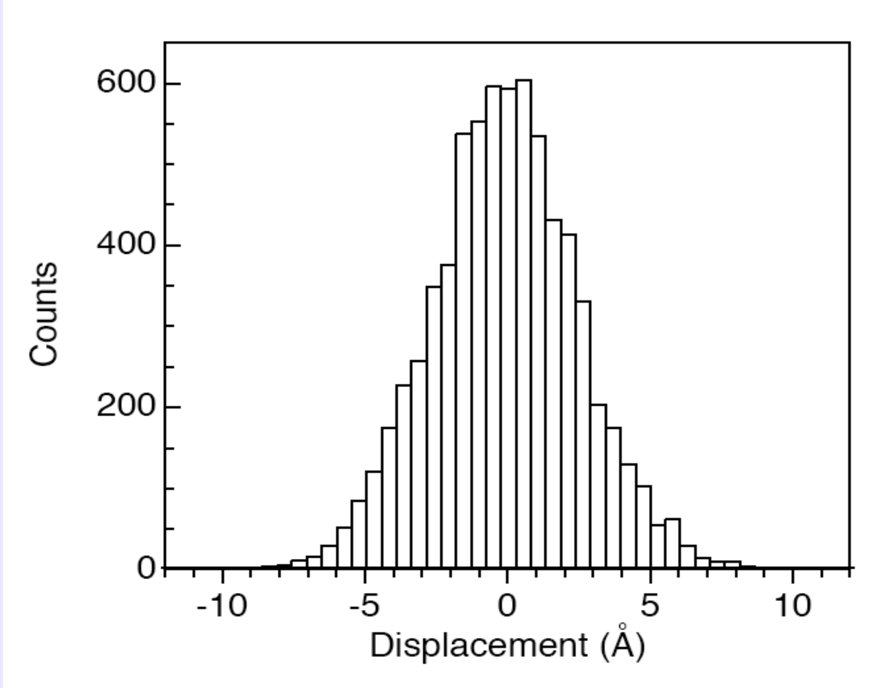
T= 4.8 K Hopping time: 0.3 s



21 nm x 23 nm (10 pA @ -100 mV)

Analysis of the thermal motion of Ce adatoms at 4.8 K



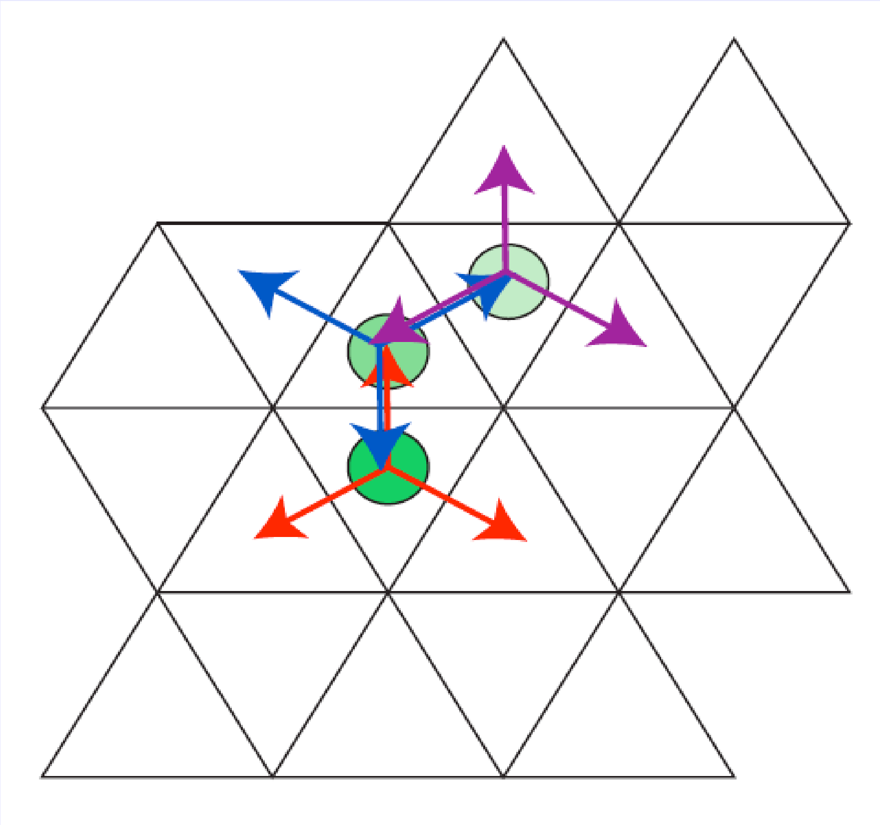


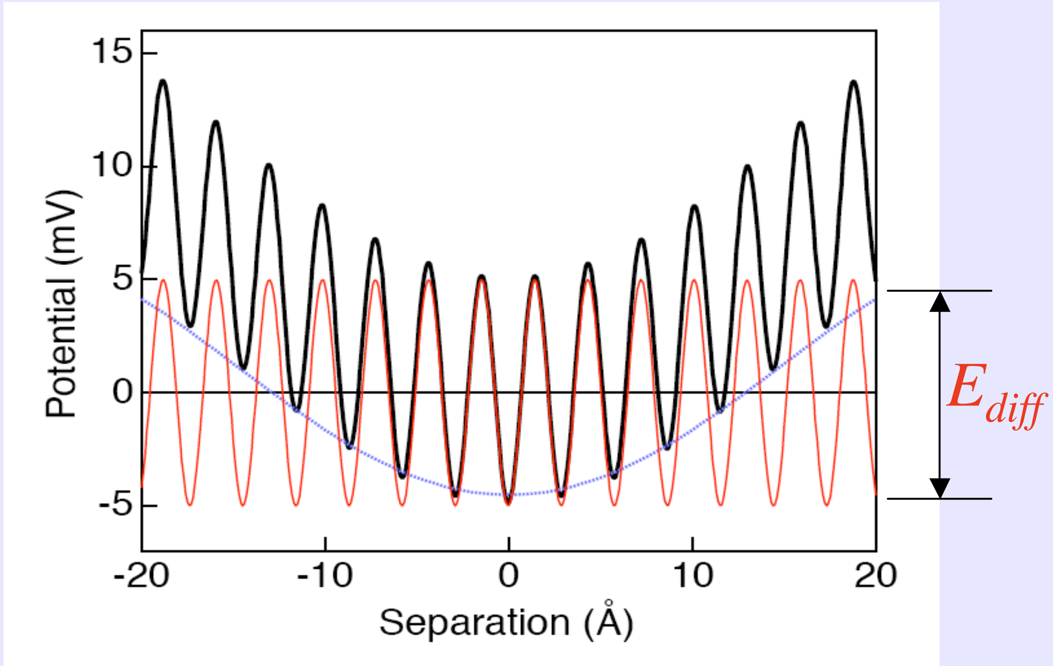
100 Å

270 Å x 270 Å
V = +100 mV, I = 5 pA

Histogram of Ce displacements
(~ 3700 cross-sections)
in their superlattice sites at 4.8 K

Surface diffusion of adatoms

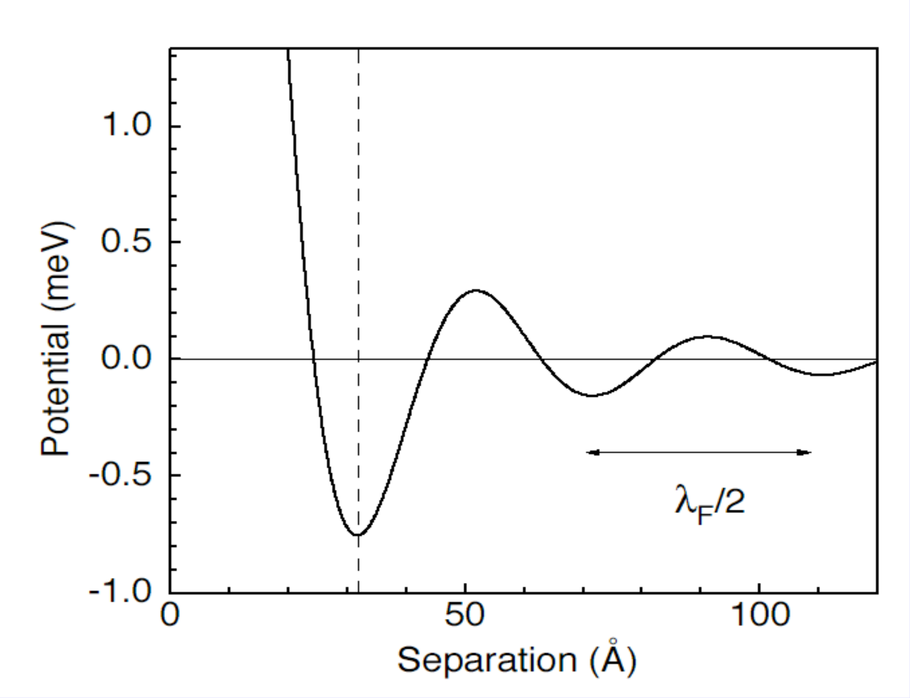




Arrhenius: $$\nu = \nu_0 \exp\left(-\frac{E_{diff}}{k_B T}\right)$$

Pair potential between two adatoms

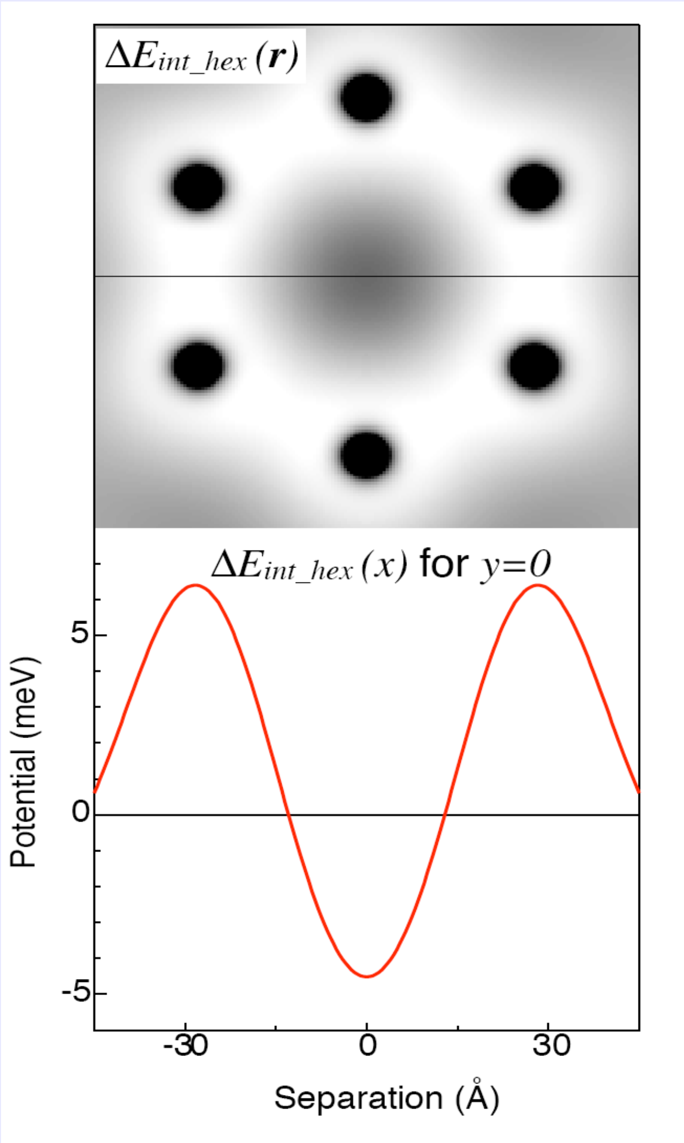
$$\Delta E_{int}(r) \simeq -AE_0 \left(\frac{2\sin(\delta_0)}{\pi}\right)^2 \frac{\sin(2k_F r + 2\delta_0)}{(k_F r)^2}$$



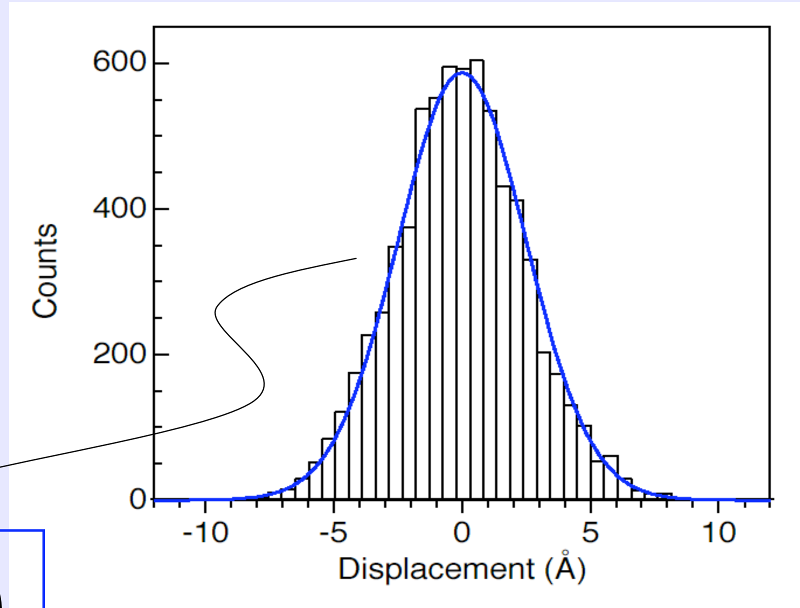
E_0: energy of the surface state onset
k_F: wavevector at E_F
δ_0 : phase shift at E_F
A : scattering amplitude

P. Hyldgaard and M. Persson,
J. Phys.: Condens. Matter 12, 13 (2000).

Analysis of the thermal motion of Ce adatoms at 4.8 K



$$\Delta E_{int}(r) \simeq -A E_0 \left(\frac{2\sin(\delta_0)}{\pi}\right)^2 \frac{\sin(2k_F r + 2\delta_0)}{(k_F r)^2}$$



$$\propto \exp\left(-\frac{\Delta E_{int\_hex}(x)}{k_B T}\right)$$

$$A = 0.26 \pm 0.03$$

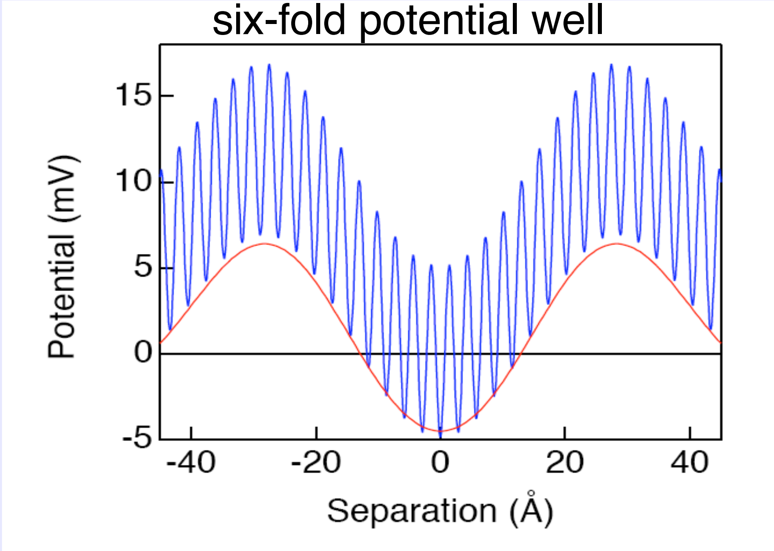
Analysis of the thermal motion of Ce adatoms at 4.8 K

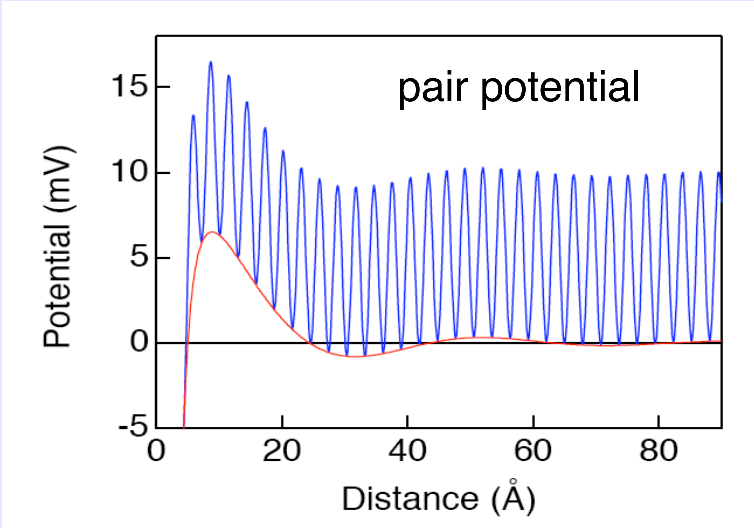
$$\tau_{diff} = 300 \text{ ms} \;\; (\nu = 3.33 \text{ Hz}) \;@\; 4.8\text{K}$$

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

$$\nu_0 \approx 10^{12}\text{Hz}$$

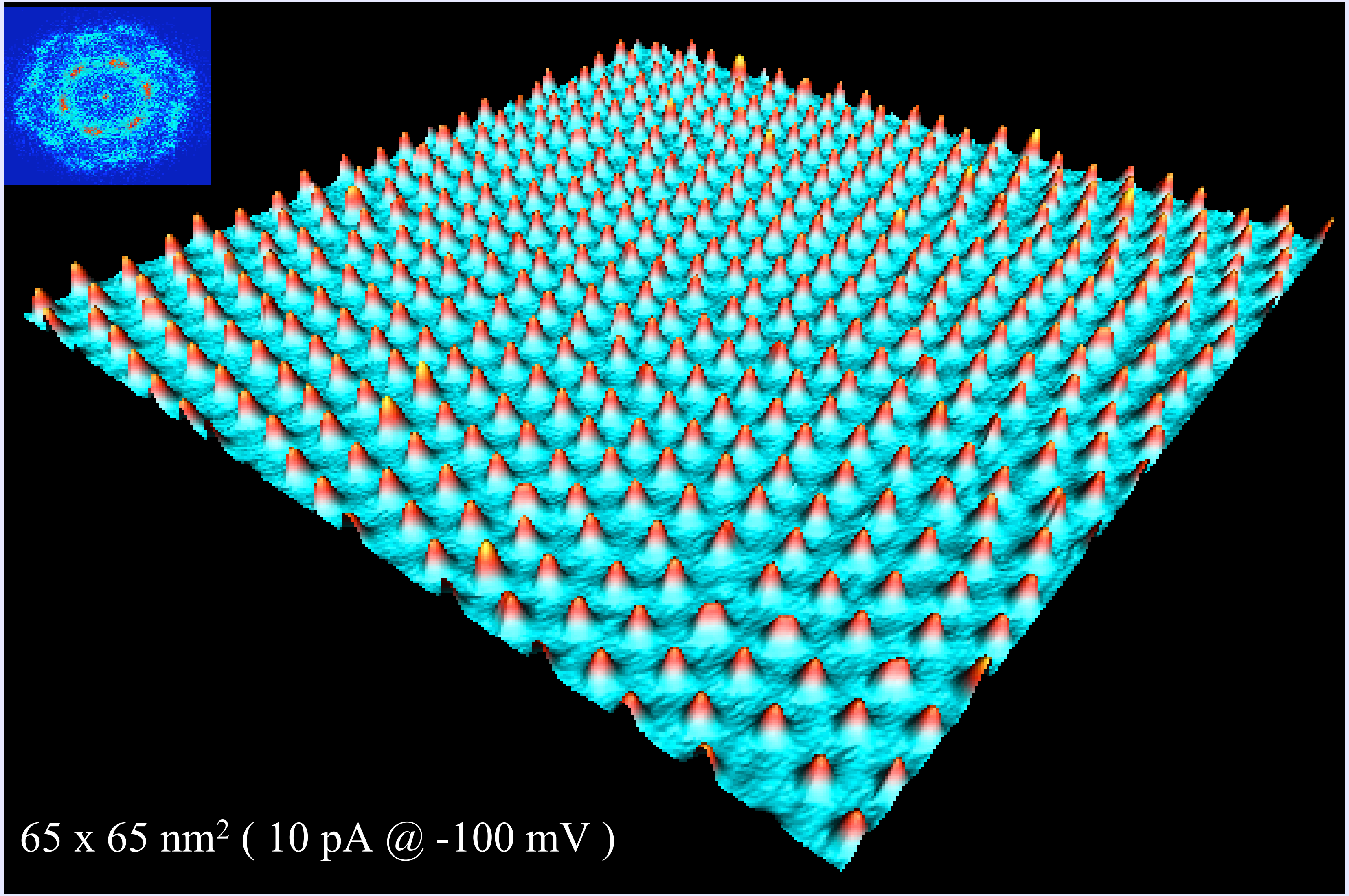
$$E_{diff} \approx 10 \text{ meV}$$





- Very low diffusion barrier for Ce/Ag(111)
- Same order of magnitude as the superlattice confining well

Ce adatom superlattice at 3.9 K



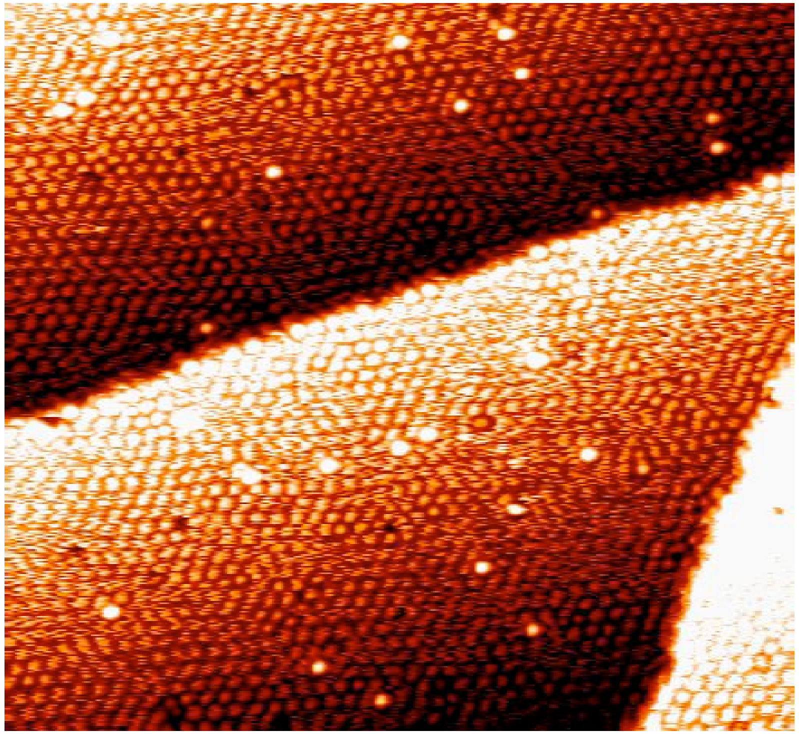
To summarize:

- Self-assembly of a 2D hexagonal Ce superlattice mediated by Ag(111) surface state electrons
- Analysis of the thermal motion of the Ce adatoms in their superlattice site
- Determination of the confining potential for the Ce adatoms in the superlattice

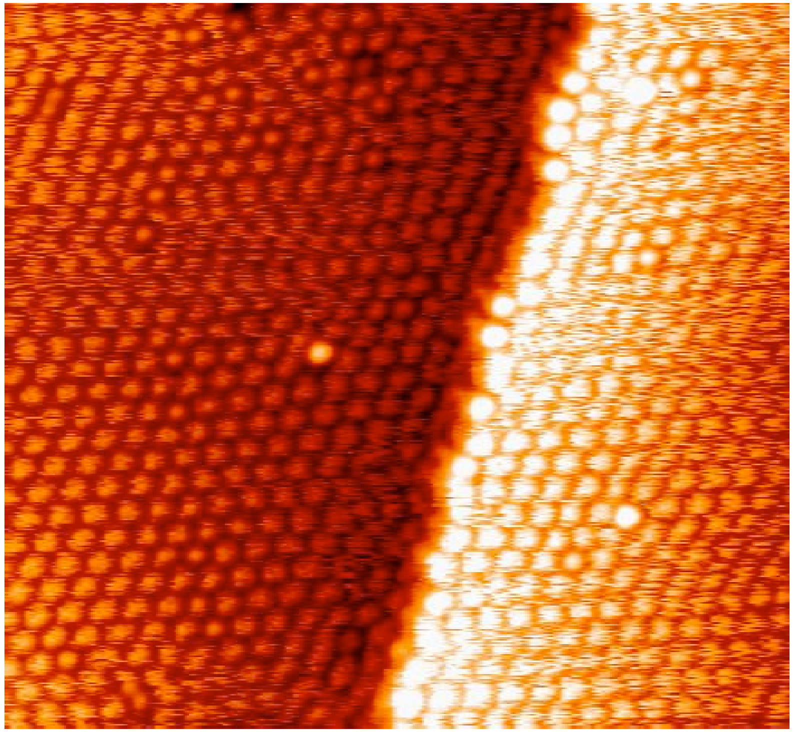
F. Silly, M. Pivetta, M. Ternes, F. Patthey, J. P. Pelz, WDS, PRL **92**, 016101 (2004)

Next........

Ce superlattice on Cu(111)



60x60nm², +1V, 3pA



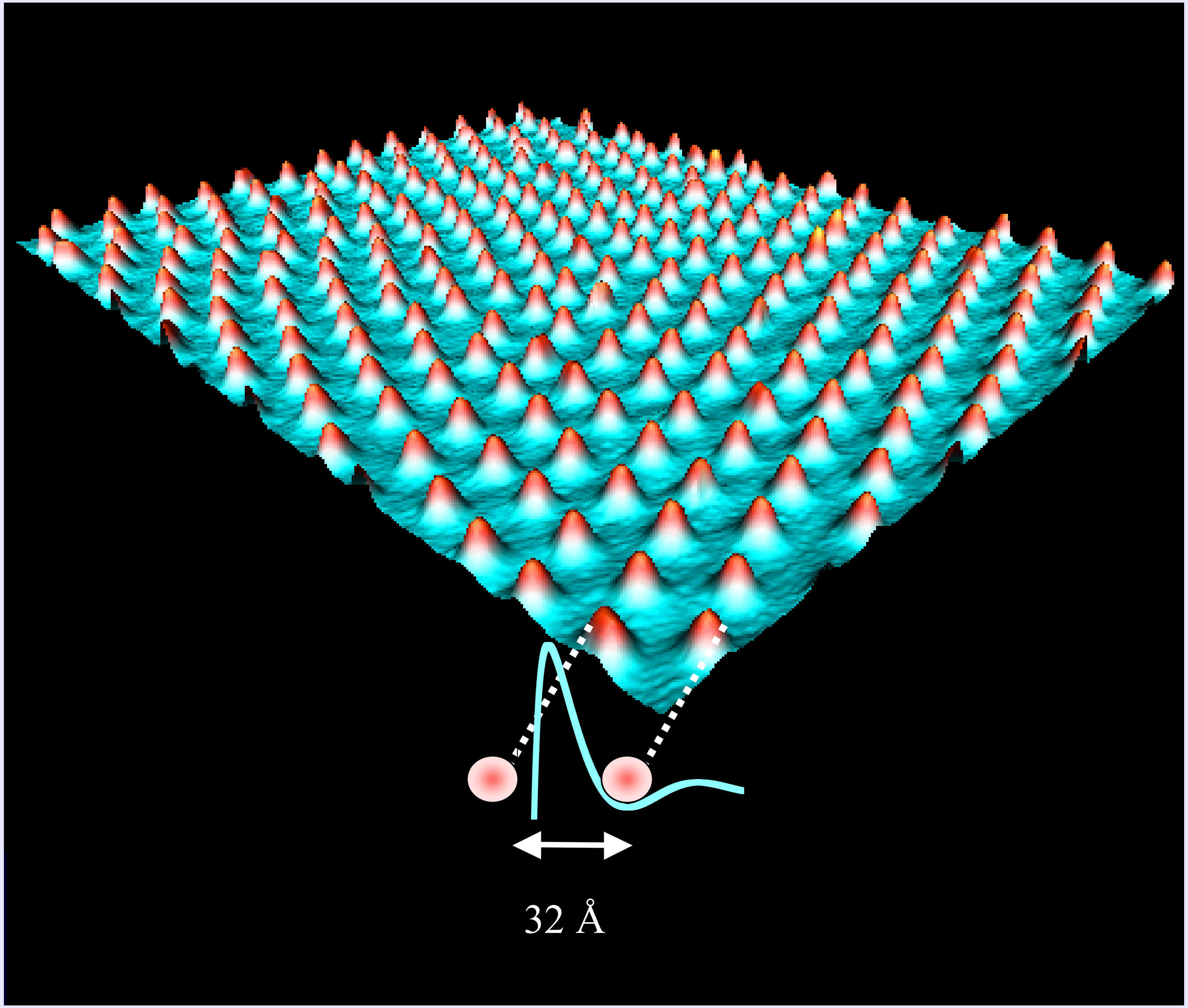
36x36nm², +1V, 3pA

Ce-Ce distance approx.: 1.5nm, corrugation approx.: 70pm

M. Ternes et al., preliminary results

Outlook:

Detecting magnetic impurities with a superconducting tip

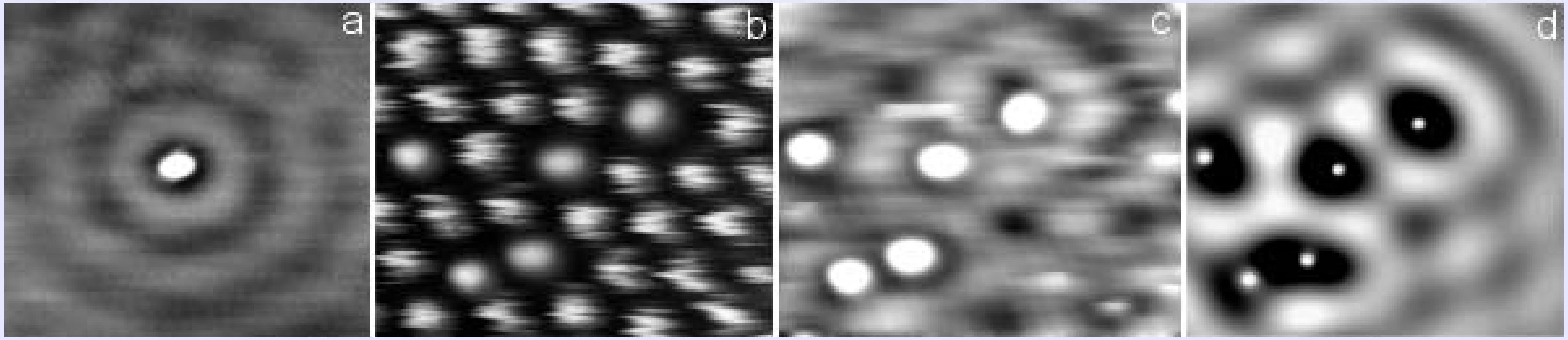


2D Kondo lattice of Ce adatoms on Ag(111)

Thank you
for your attention!

Standing wave patterns of Ce adatoms and dimers on Ag(111)

$21\ nm^2$	20 x 17 nm	20 x 17 nm	20 x 17 nm



Isolated Ce adatom -3 mV, 19 pA	Superlattice -100 mV, 30 pA	Ce dimers -3 mV, 20pA	Calculated electron density
T = 3.9 K	T = 4.8 K	T = 4.8 K	

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

F. Silly, M. Pivetta, M. Ternes, F. Patthey, J. P. Pelz, WDS, PRL, in print

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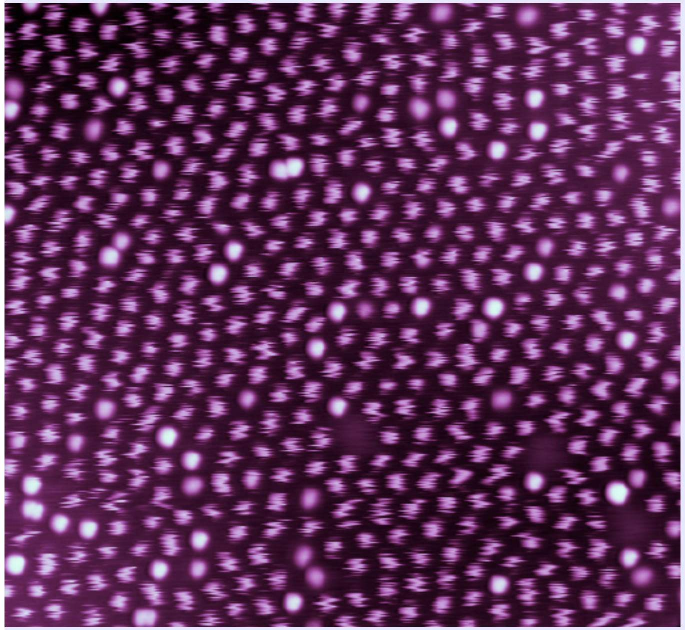
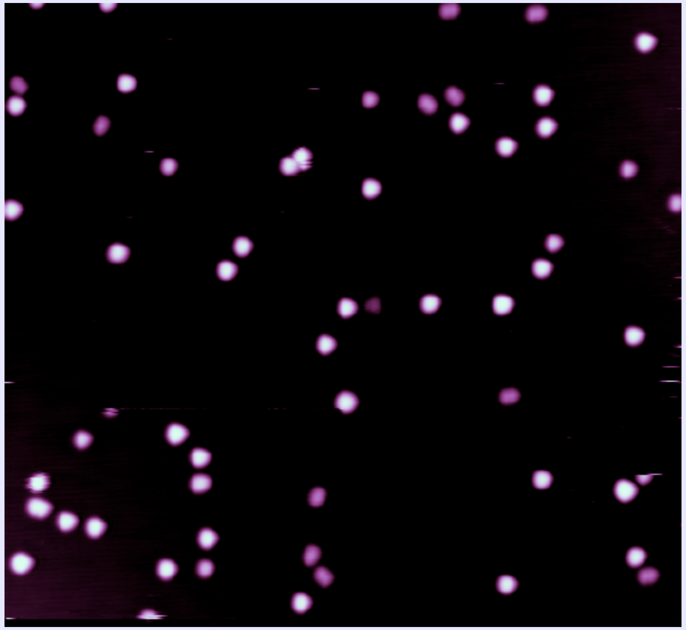
Superlattice/surface interaction at 4.8 K

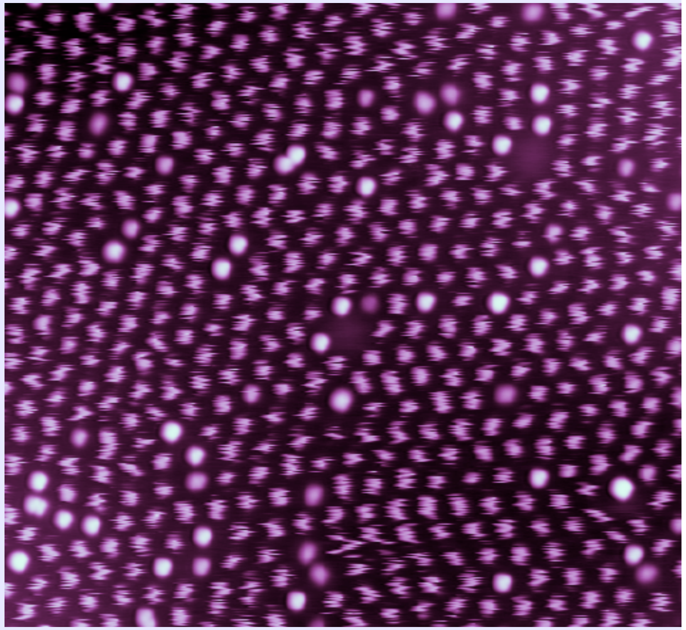
67 x 67 nm^2



*50 pA @ **-100 mV***



*50 pA @ **1.2 V***



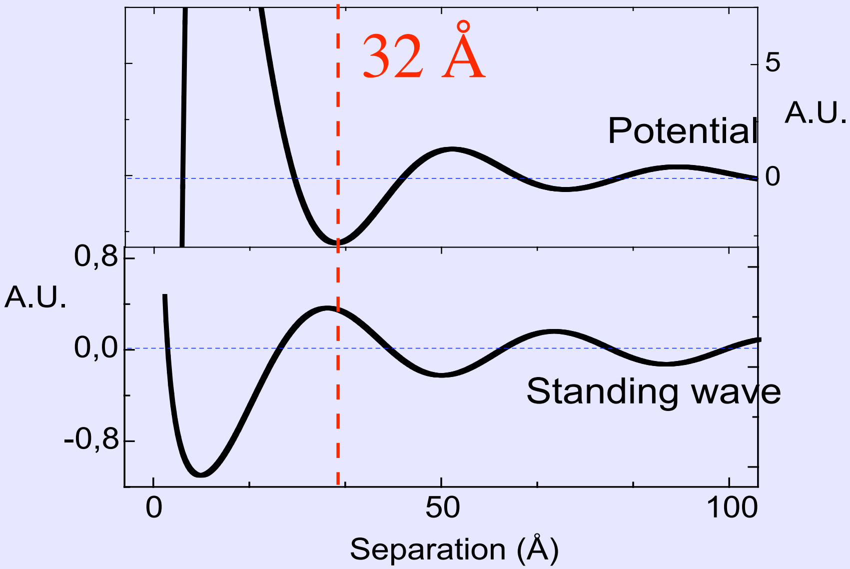
*50 pA @ **-100 mV***

Low Ce-adatom adsorption energy
Adatom-adatom repulsion
No Ce-dimer creation

Two body interaction induced by surface state electrons: Ce/Ag(111)

$$\Delta E_{\text{int}}(\rho) \approx -E_0 \left(\frac{2\sin(\delta_0)}{\pi} \right)^2 \frac{\sin(2k_F\rho + 2\delta_0)}{(k_F\rho)^2}$$

P. Hyldgaard and M. Persson, J. Phys.: Condens. Matter **12**, L13 (2000).



Ce/Ag(111):

$\delta_0 = 0.37\ \pi$

$E_0 = -\ 63$ meV

$k_F = 0.813\ nm^{-1}$

First minimum in the potential located at 3.2 nm from Ce adatom

1 % of a ML of Ce on Ag(111) @ 4.8 K near a step edge

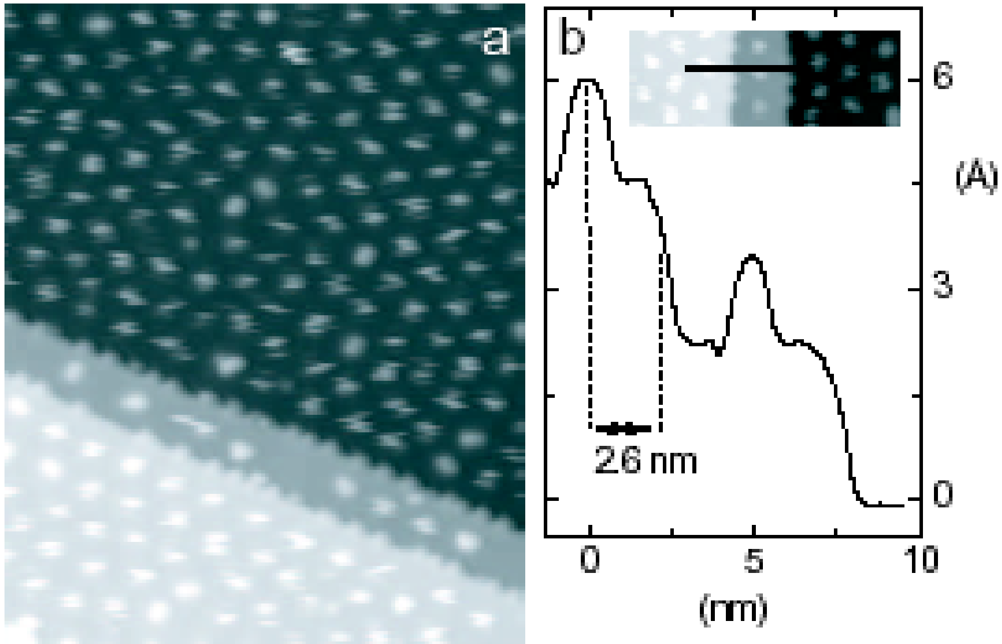
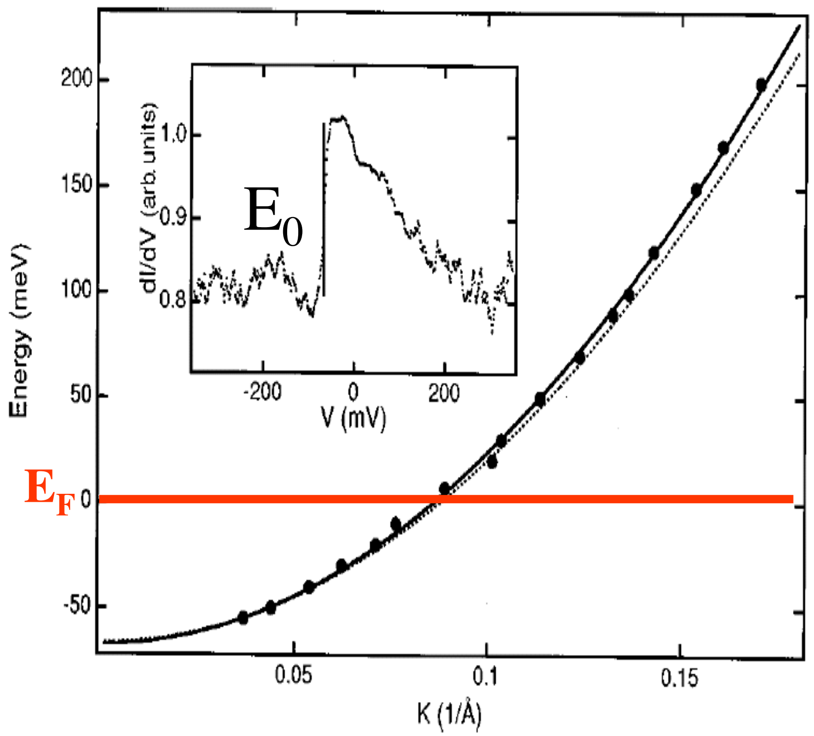
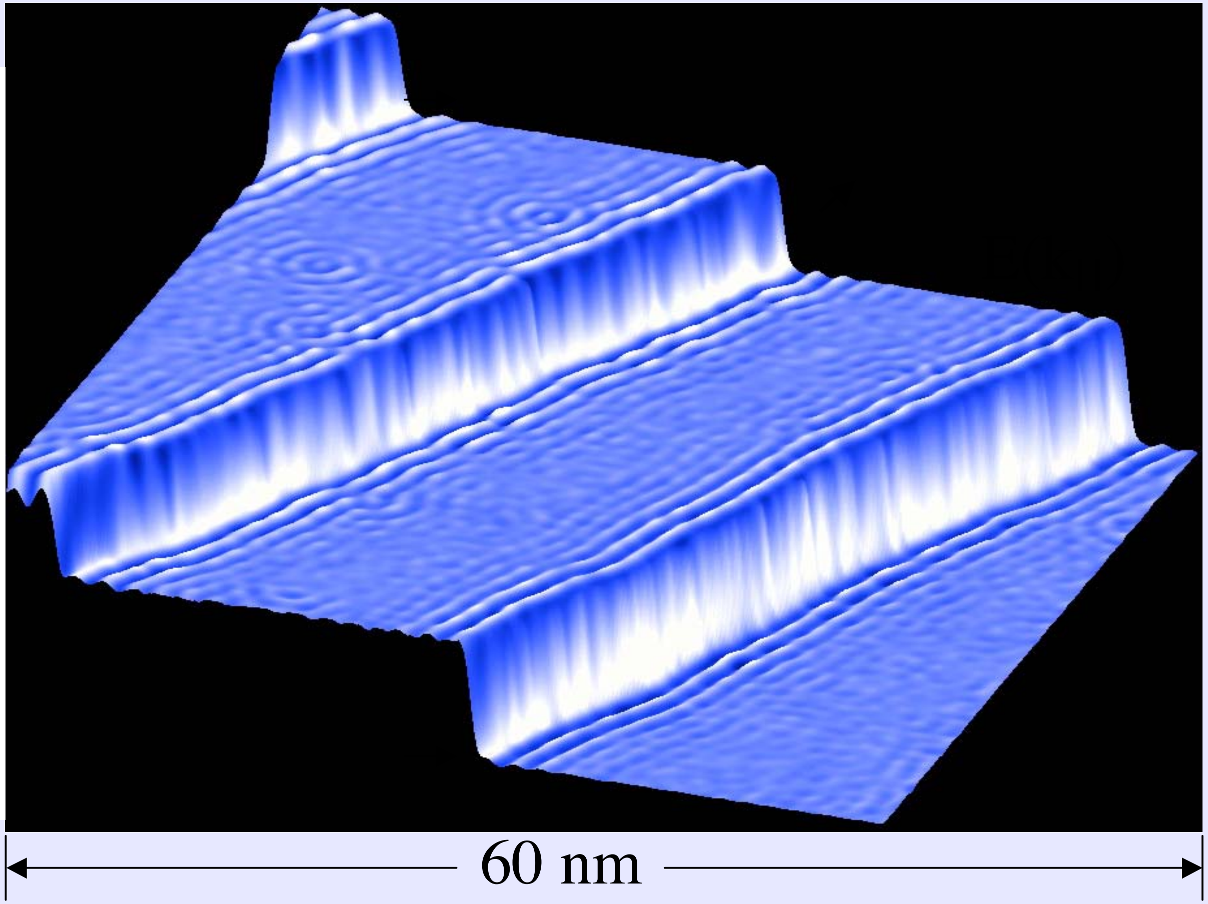


FIG. 8: (a) 38 × 53 nm^2 STM-image Ce adatoms near step edge of Ag(111) at 4.8 K (U_s = −100 mV, I_s = 30 pA). (b) Line profile taken perpendicular to step edge (see inset).

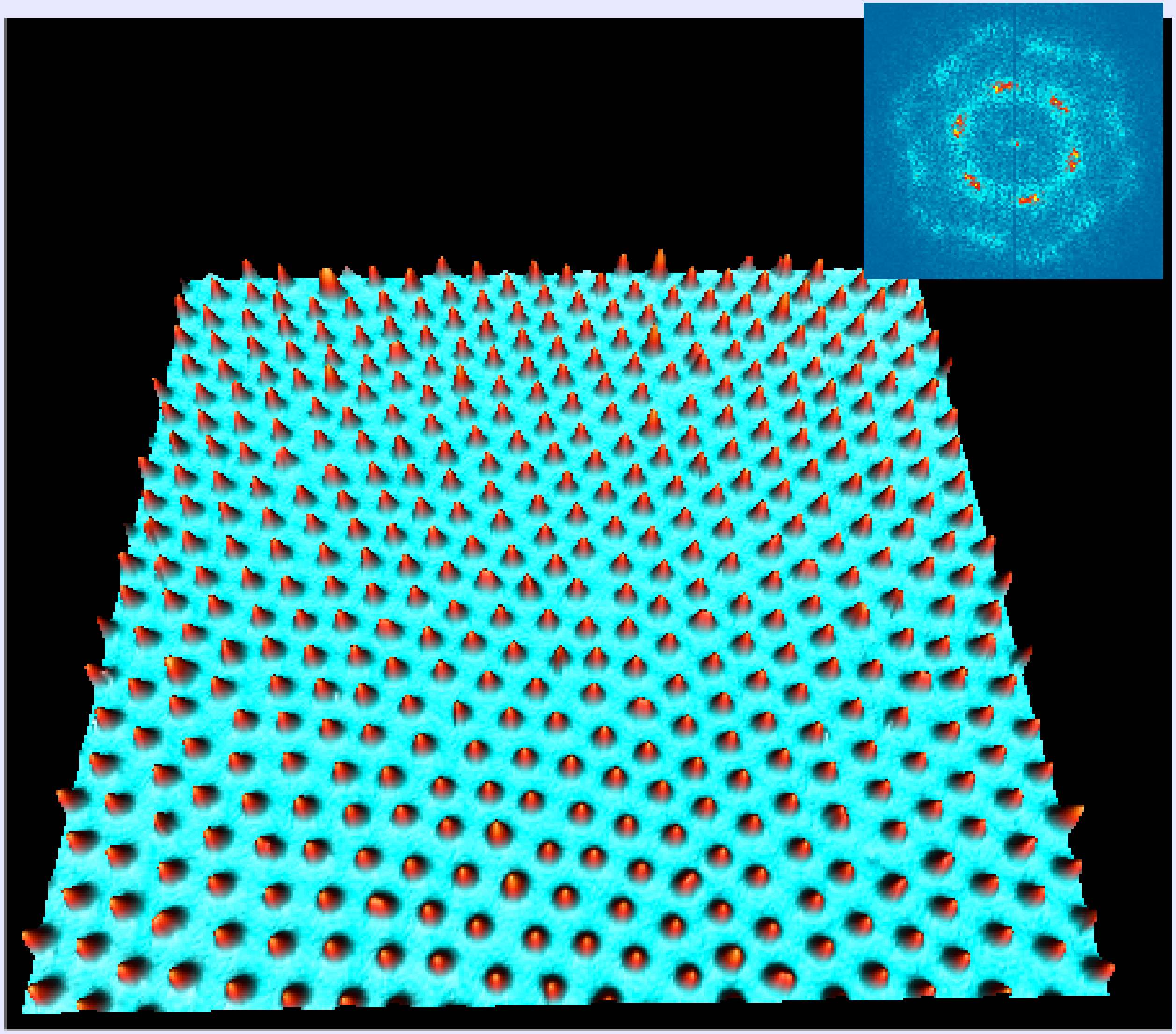
Electron standing waves on Ag(111) @ 5 K





J. Li et al., PRB **56**, 7656 (1997)

Self-assembled superlattice of Ce adatoms on Ag(111)



64 nm^2
100mV, 10pA
T = 3.9 K

F. Silly et al., submitted

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