Quasicrystalline metallic adlayers

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Solids

Amorphous

Lack of order

Crystalline

Periodic long range order, limited number of allowed rotational symmetries

Quasicrystalline

Aperiodic long range order

Forbidden rotational symmetry (5f, 8f, 10f and 12f)

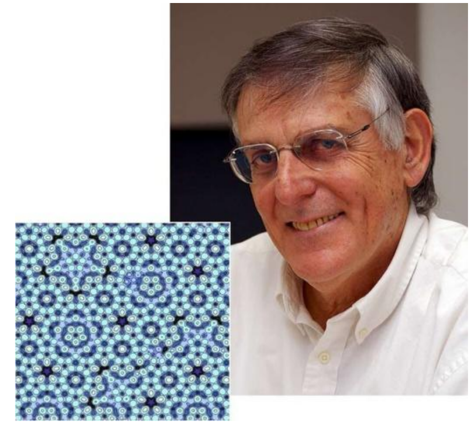
Sharp diffraction pattern

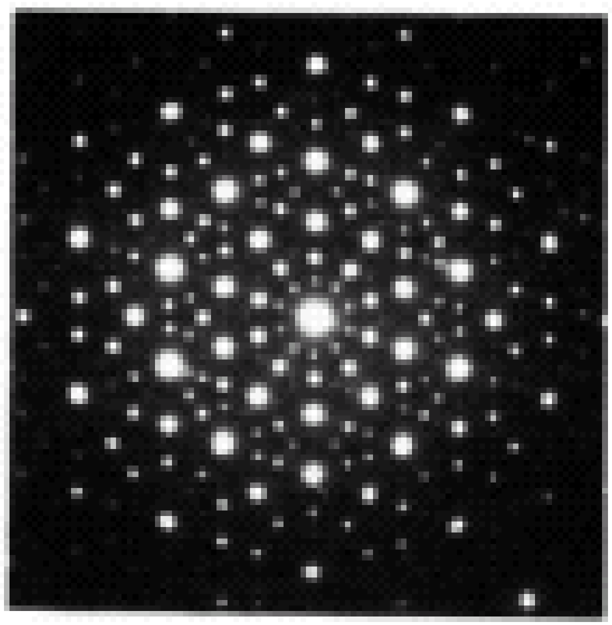
Discovery of quasicrystals

D. Shechtman, I. Blech, D. Gratias, J. W. Kahn,

Phys. Rev. Lett. 53, 1951 (1984)

Prof. Shechtman awarded Nobel prize for discovery of quasicrystal in 2011





Selected area electron diffraction pattern of icosahedral phase Al-14 at. % Mn alloys along fivefold axis.

As for the definition of a crystal, in 1992 the International Union of Crystallography changed its definition of a crystal from a regular repeating array of atoms to "any solid having an essentially discrete diffraction pattern."

Many quasicrystals have been discovered since 1984 (Al-Pd-Mn, Al-Cu-Fe,Al-Li-Cu, Al-Mn-Si,Al-Cu-Ru,Al-Pd-Re, Al-Ni-Co, Cd-Yb, Al-Ni-Co….)

$Al_{63}Cu_{24}Fe_{13}$ quasicrystal have been found in nature: a mineral discovered 3 years ago in the Koryak Mountains in eastern Russia. (**Evidence for the extraterrestrial origin of a natural quasicrystal,** L Bindi et al, **PNAS, 109, 1396, 2012)**

But no elemental metal has been observed in the quasicrystalline phase....

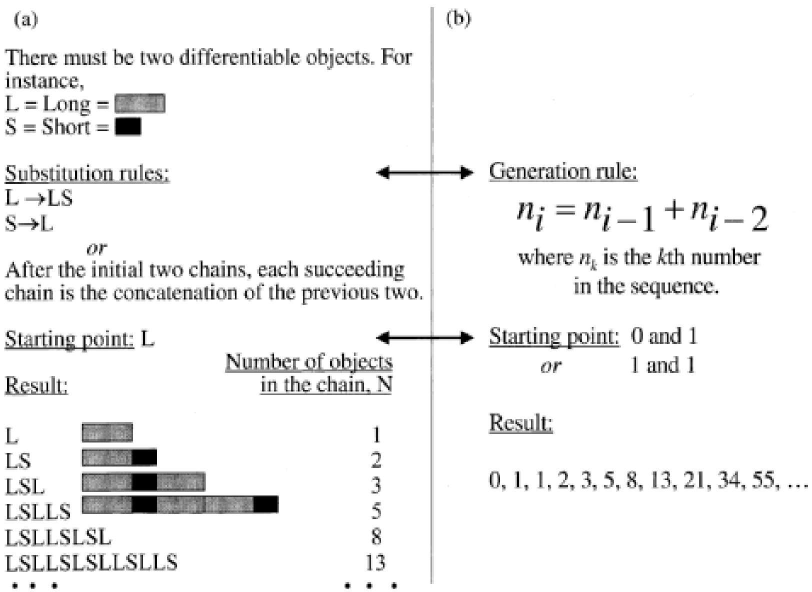
High resistivity, -ve temperature cofficient
Low electronic contribution to specific heat
Low thermal conductivity
Low frictional coeffcient
Low wettability
Stabilized by pseudogap near Fermi level.

Quasicrystals used in one of the world's most durable steels, made by a company in Sweden for razor blades and surgical needles.

Other applications: nonstick coatings in pans, heat insulation in engines, and as thermoelectric materials to salvage waste heat; improve the mechanical properties of engineering materials, hydrogen storage.

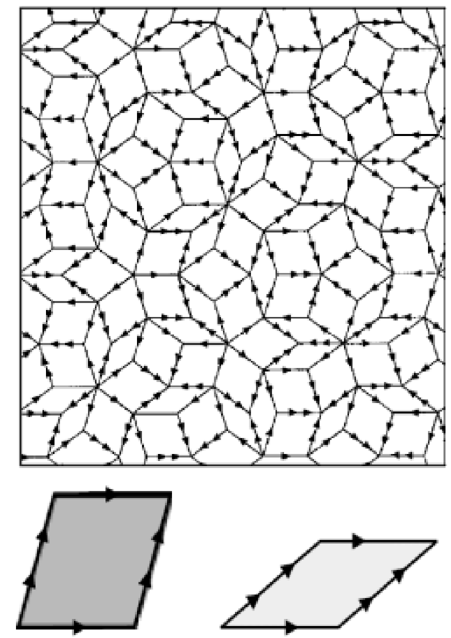
Model of quasicrystals

The Fibonacci Sequence: 1-D quasiperodic chain



If L/S is irrational → No periodicity in chain. In Fibonacci chain, irrational ratio is golden mean τ = 1.618….

Penrose Tiling: 2-D quasiperiodic systems



72° fat rhombus   36° skinny rhombus

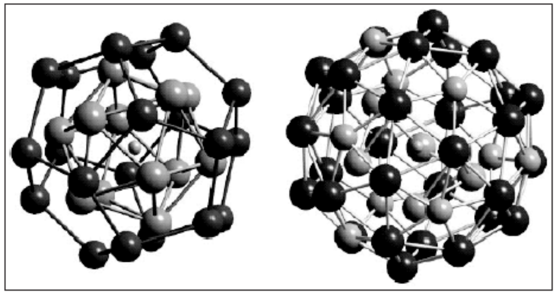
The lattice is created from at least two building blocks and the blocks are tiled according to the given rule → Penrose tiling.

Origin of quasicrystallinity: stability provided by the pseudogap

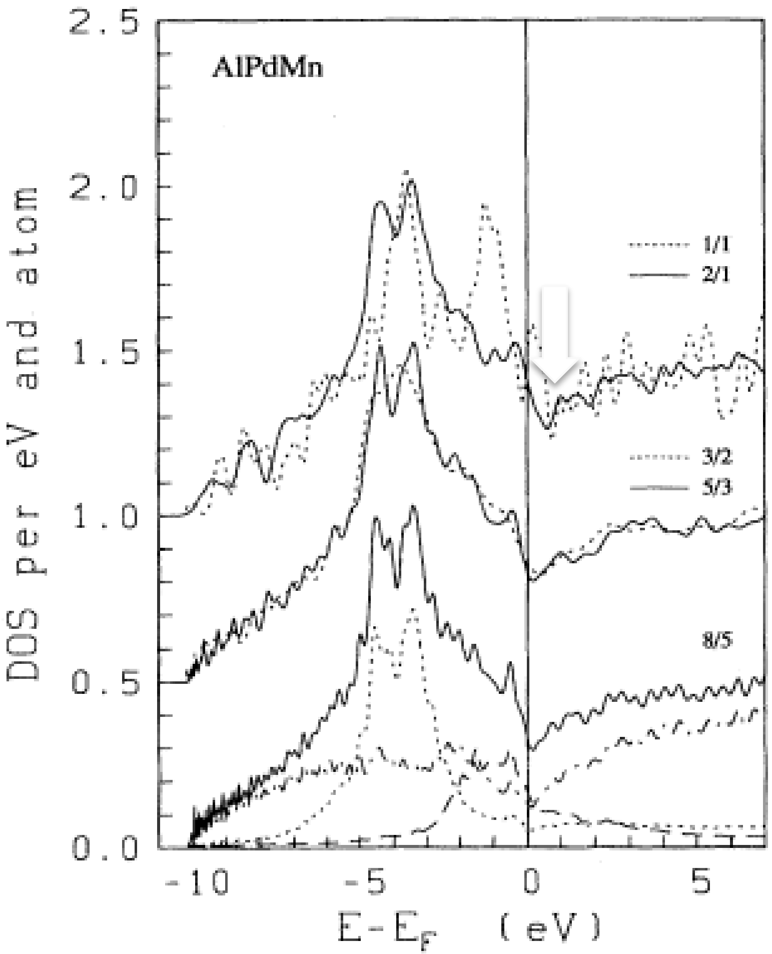
Pseudogap: Minimum in the density of states (DOS) near to E_F.

✓The pseudo Brilloiun zone in QC's determined from the strongest peaks in the diffraction pattern is almost spherical due to high symmetry of i-point group.

✓Optimal matching of PBZ and FS results in pseudogap at E_F.

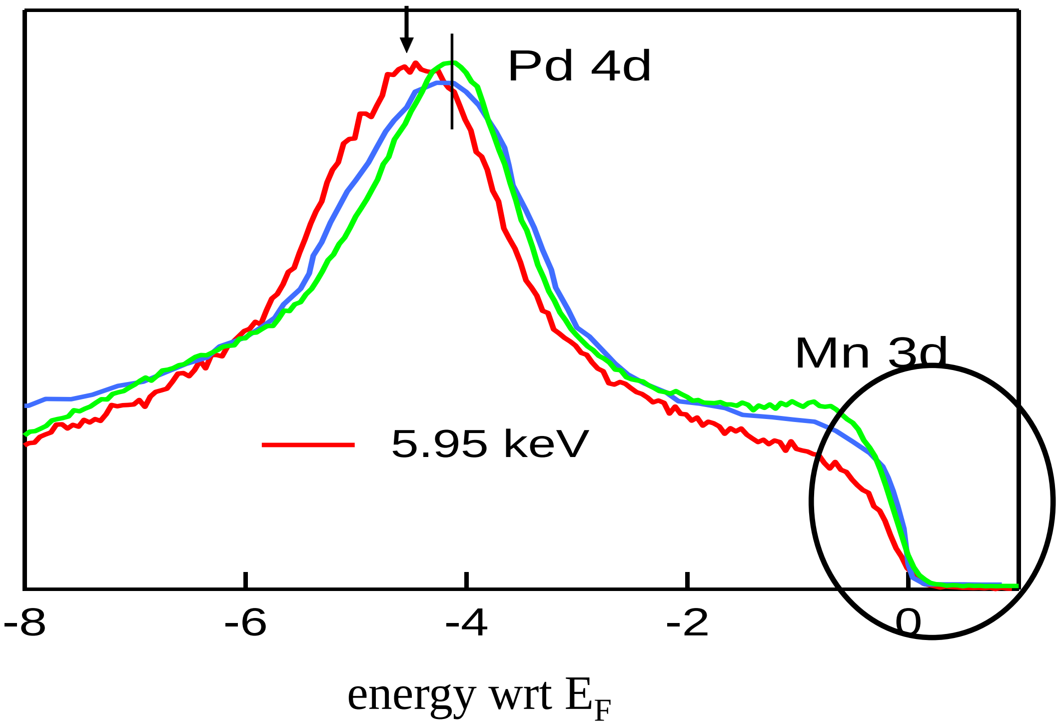


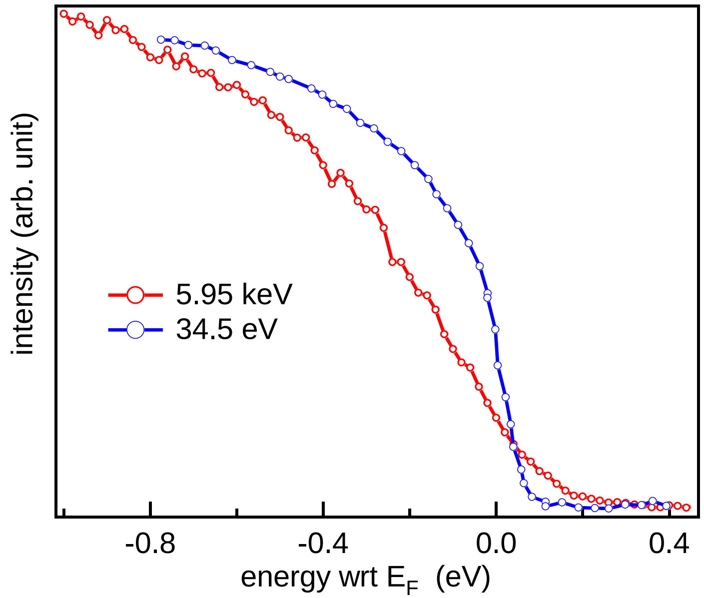
Pseudo-Bergman cluster (left) and pseudo-Mackay cluster (right) found in *i*-QC containing 33 and 50 atoms respectively.



M. Krajci et al., PRB 51, 17355 (1995)

Pseudogap in bulk by hard x-ray photoemission



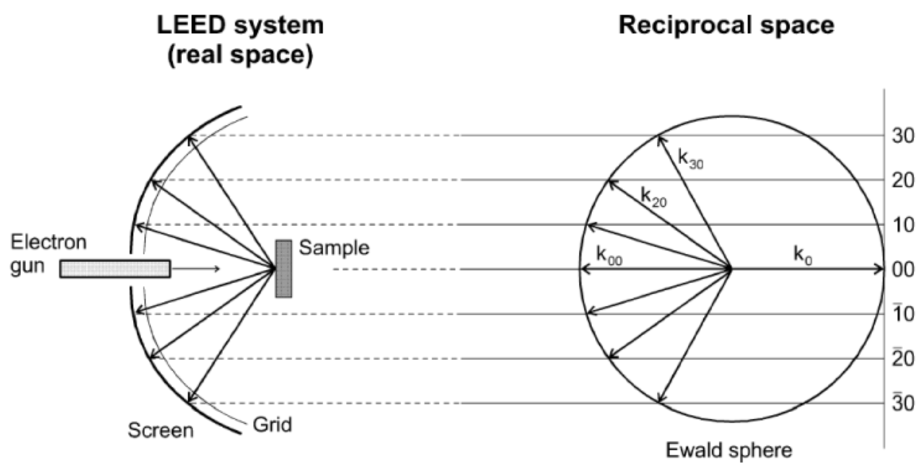


- Evidence of deepening pseudogap
- Fermi edge not observed in bulk

J. Nayak, A. Rai, S. Singh, P. Rajput, M. Maniraj, J. Zegenhagen, D. L. Schlagel, T. A. Lograsso, K. Horn, and S. R. Barman (submitted)

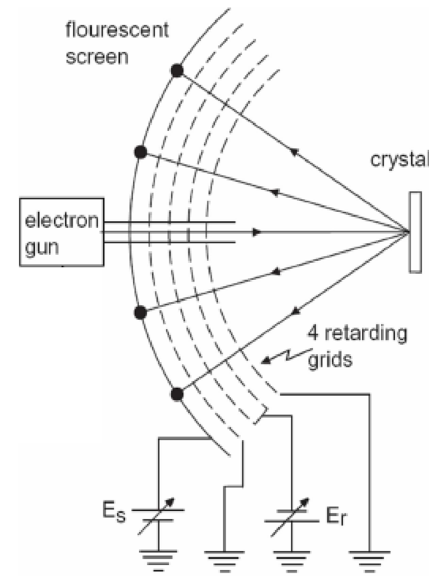
The surface of the quasicrystals: can we directly observe the forbidden symmetries?

Low Energy Electron Diffraction (LEED)



Real space

Reciprocal space



Experimental arrangement

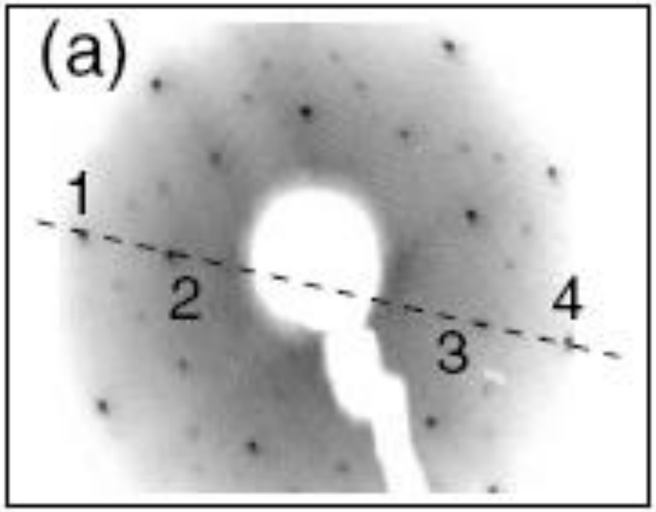
Electrons coming from gun are diffracted due to their wave character at the surface.

Only elastically scattered electrons contribute to diffraction pattern on the screen.

LEED is very surface sensitive due to limited mean free path of low energy electrons (20-200 eV).

Provides direct image of surface reciprocal lattice.

LEED on quasicrystal surfaces



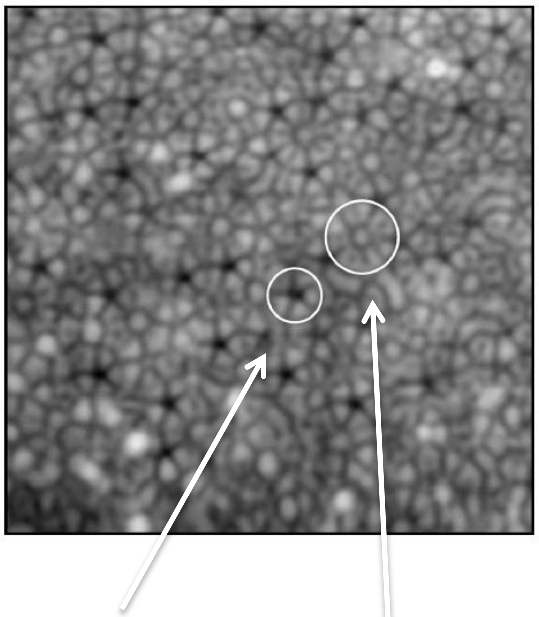
Al-Pd-Mn LEED pattern.

Five fold symmetry observed on the five fold surface of i-Al-Pd-Mn

Scanning tunneling microscopy images of quasicrystal surfaces

i- Al-Pd-Mn

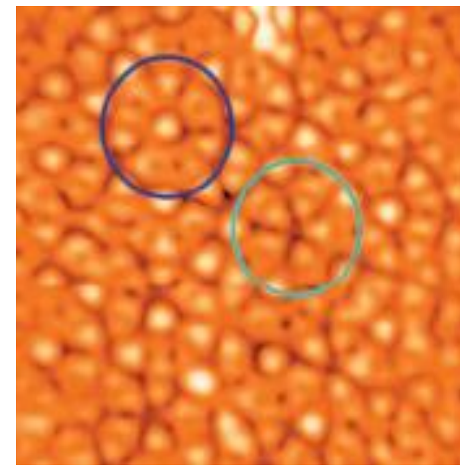
M. Krajčí, J. Hafner, J. Ledieu, and R. McGrath, Phys. Rev. B. 73, 024202 (2006).



Dark star White flower

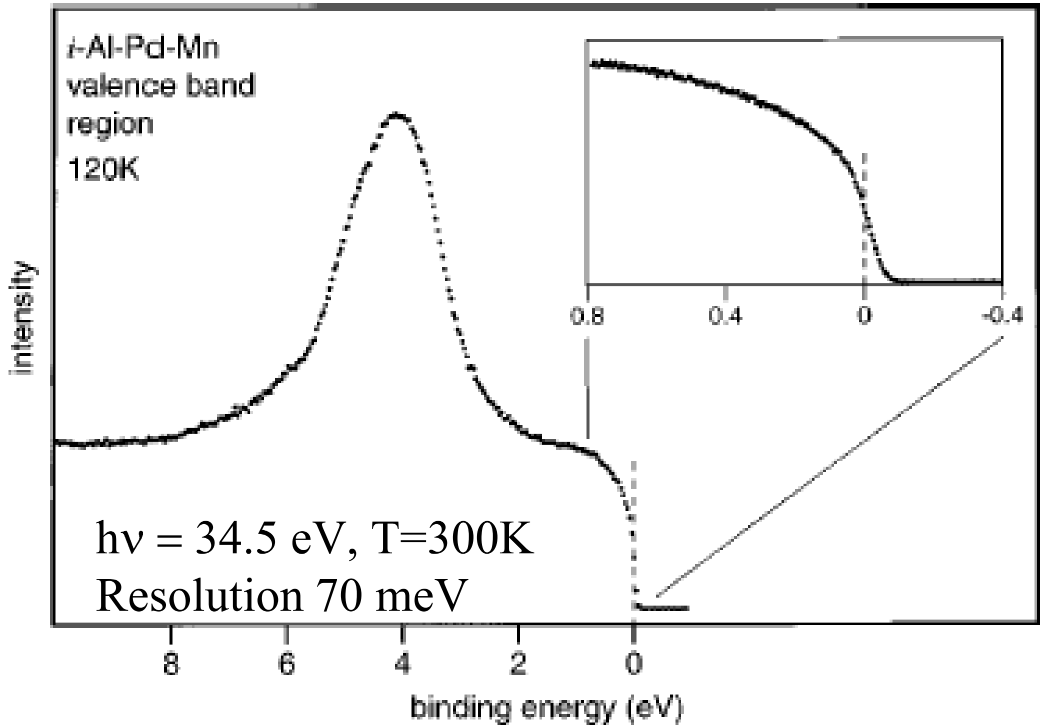
Al-Ni-Co

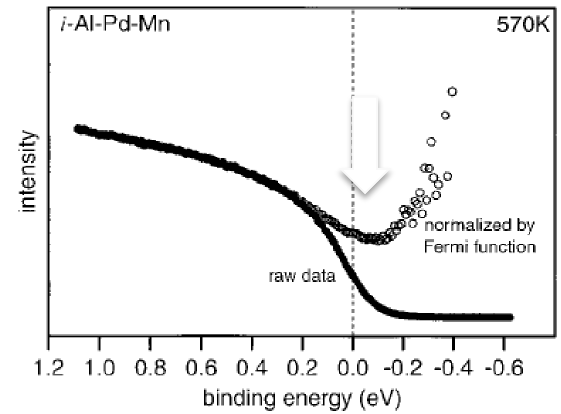
Widmer et al.,Phys. Rev B, 79, 104202 (2009)



STM image at 5 K (8×8 nm^2)

Soft x-ray photoemission of Al-Pd-Mn





Signature of pseudogap close to E_F.
Surface more metallic than the bulk .

G. Neuhold, S. R. Barman, K, Horn, W, Theiss, Ph. Ebert, K, Urban, Phys. Rev. B 58, 734 (1998)

Metal adlayers on quasicrystals:

Metal-quasicrystal heteroepitaxy

Most quasicrystals are complex ternary alloys → Explanation of growth, structure and physical properties is not easy → Need for quasicrystals with reduced complexity.

↓

Use quasicrystal surfaces as growth templates for metals

Single element quasicrystal film

Opportunity to study the impact of quasicrystallinity independently of the complex alloy composition of thermodynamically stable bulk phase

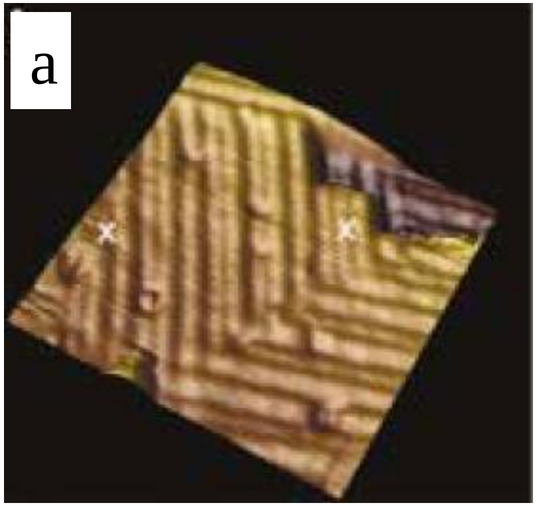
Sb, Bi, Cu, Sn found to be quasiperiodic.

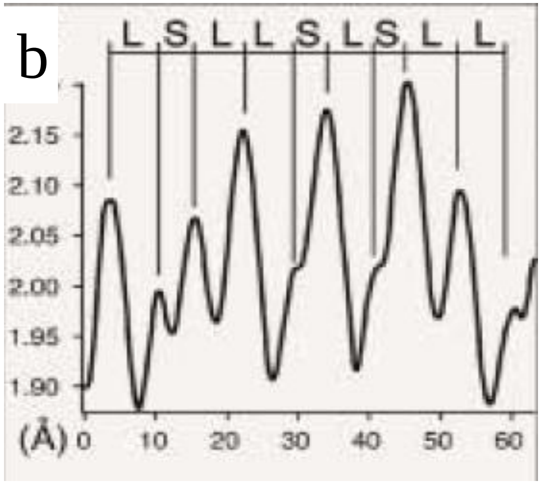
3-D metal island nucleation at specific sites of QC substrate

Surface patterning

Example: Cu forms pseudomorphic films on Al-Pd-Mn

Lindeau et al., Phys. Rev. Lett., 92, 135507 (2004)





(a) STM image (100x100 A) after 5.5 ML deposition (b) A profile between the points marked in (a)

LEED pattern at energy 50 ev after 5.5 ML deposition

Alkali metal adlayers on i-Al-Pd-Mn: studies using photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED)

How the experiments were performed?

A. 4-level UHV chamber (donated by FHI -MPG)

B. **Low energy electron diffraction (LEED)**

C. Hemispherical electron energy analyzer

D. 4-axis manipulator (donated by FHI-MPG)

E. Load lock system

SAES getters for alkali metals,
Knudsen cell for Mn and Sn

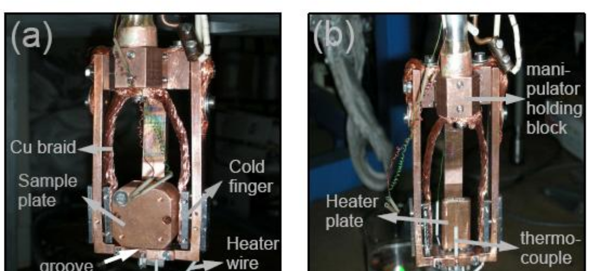
A. K. Shukla et al., Rev. Sci. Instrum,, 75, 4467 (2004);

Base pressure: 4 x 10^{-11}mbar

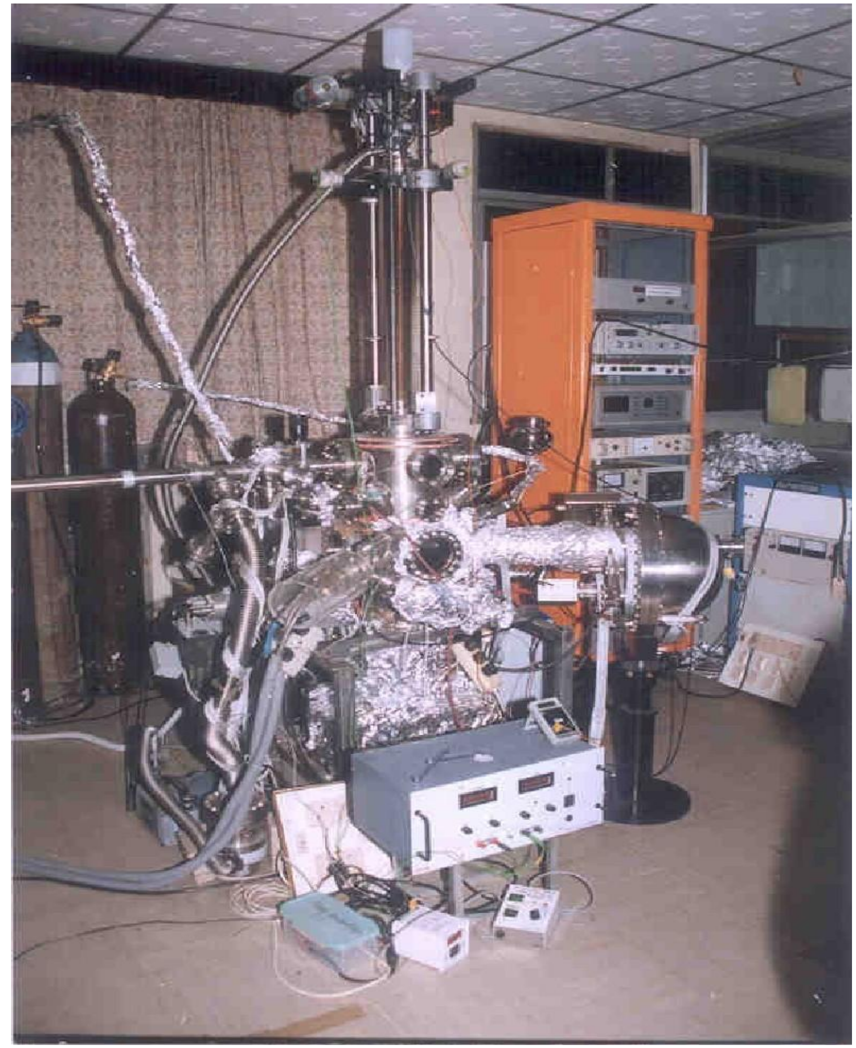
Subsatrate cleaning: Ar^{+} sputtering

Heating / cooling: 1000K / 125 K

Substrate temperature: 125 K
The atomic density of a completed monolayer is 0.067 atoms/Å^2, corresponding to θ=0.50.



R. S. Dhaka et al, Rev. Sci. Instrum, 81, 043907 (2010).



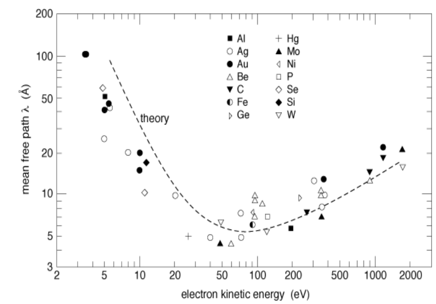
Preparation of the quasicrystal surface

Single grain specimens (i-Al69.4Pd20.8Mn9.8, i-Al63Cu25Fe12) grown by Bridgmann technique

Native oxide layer
Bulk Al-Pd-Mn crystal

Thickness of oxide layer:
* 30-40 A on Al [C.E. Aumann et al. J. Vac. Sci. Technol., B 13 1178, (1995)]
* 1250- 5000 A on aluminum alloy [Toh, S. K. et al., *Surface Review and Letters*, 10, 365 (2003-04)]

* Probing depth of XPS is about 15 A



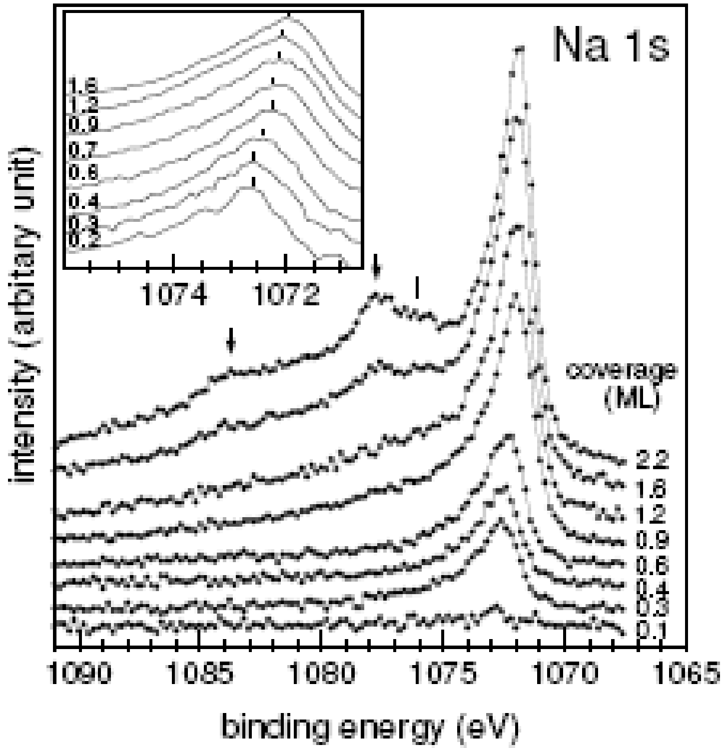
•Native oxide removed by sputtering.

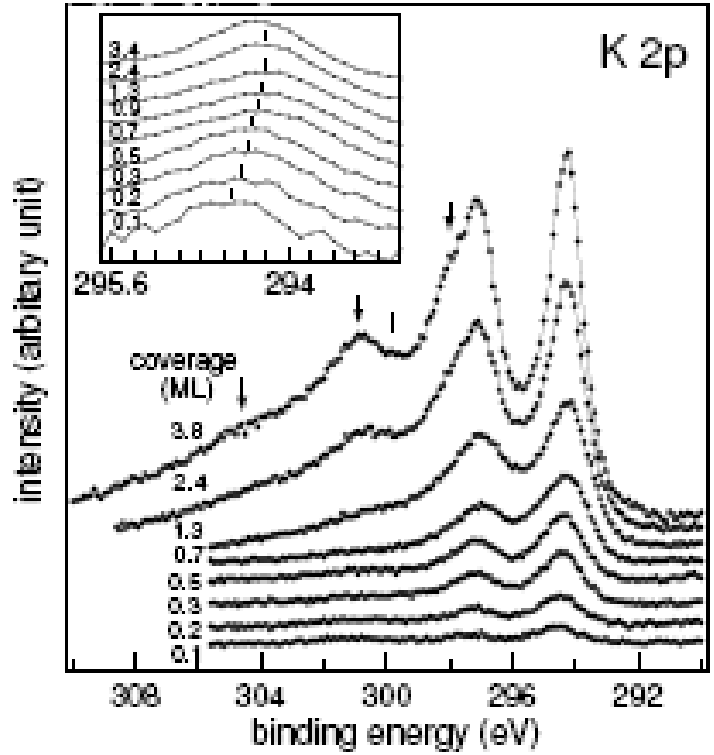
• Sputtering changes composition: Pd rich and Mn deficient surface, it is not clear down to what depth this composition gradient exists.

• So, composition restored by annealing to 620 C for AlPdMn, 710C for AlCuFe.

•For surface studies, mid 10^{-10} mbar required for annealing for oxygen free surface and obtaining LEED and reliable XPS.

Alkali metal core-level spectra as a function of coverage



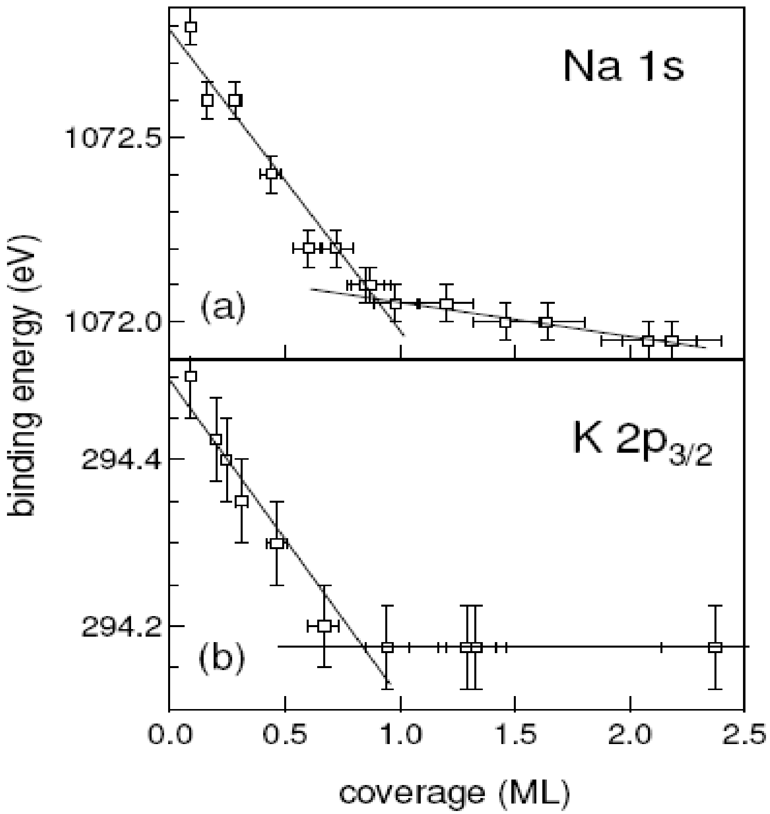


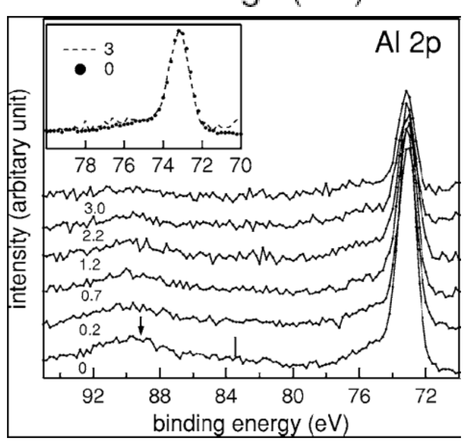
Na: $1s^2 2s^2 2p^6 3s^1$

Monotonic decrease in binding energy (BE) with increasing coverage up to 1 ML.

Plasmon features appear above 1 ML.

BE variation of alkali metal core-levels as function of coverage





No charge transfer,

covalent model.

Dispersed phase or Condensed island phase?

i-Al-Pd-Mn surface has a large surface corrugation potential
⇒condensed island phase energetically unfavorable.

Linear variation of BE up to a ML.

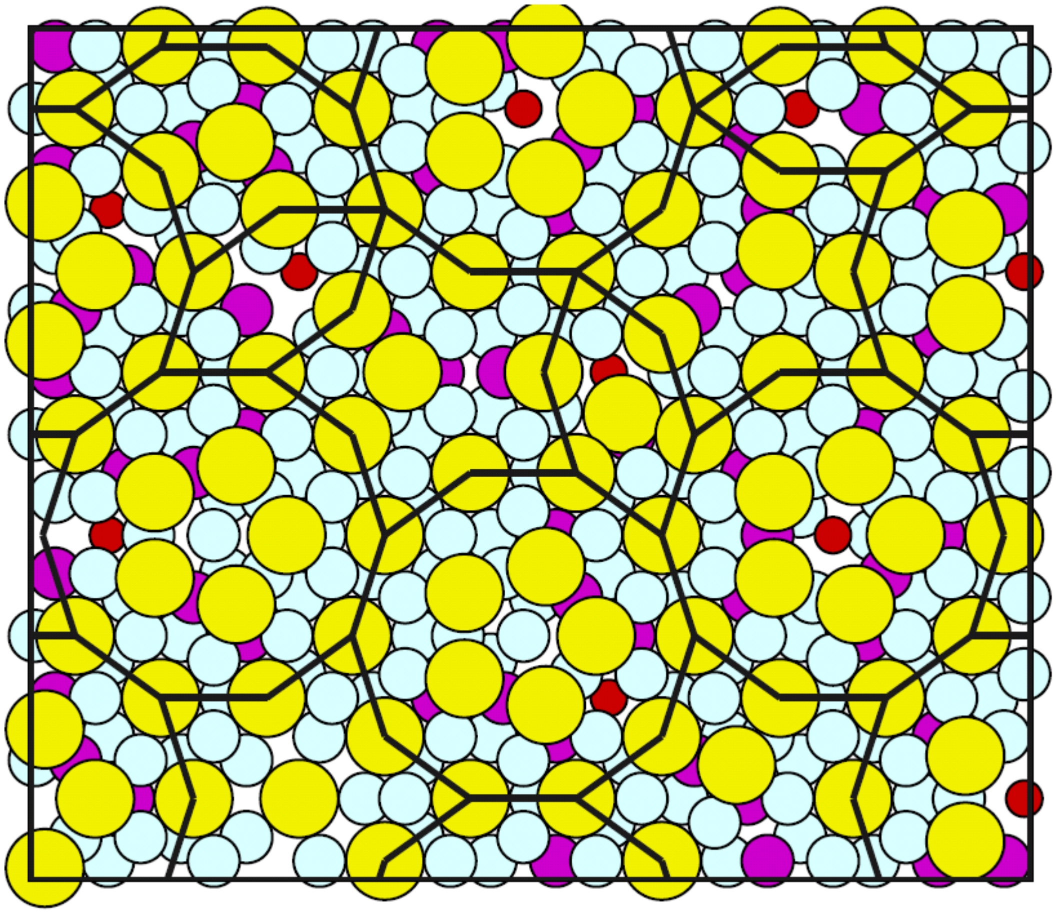
Appearance of collective excitation >1ML

⇒Dispersed phase

=> Related to QC surface morphology

A. K. Shukla et al., PRB 73, 054432 (2006).

Ab initio density functional theory of alkali metal adlayers on i-Al-Pd-Mn



Krajci and Hafner, 75, 224205 (2007)

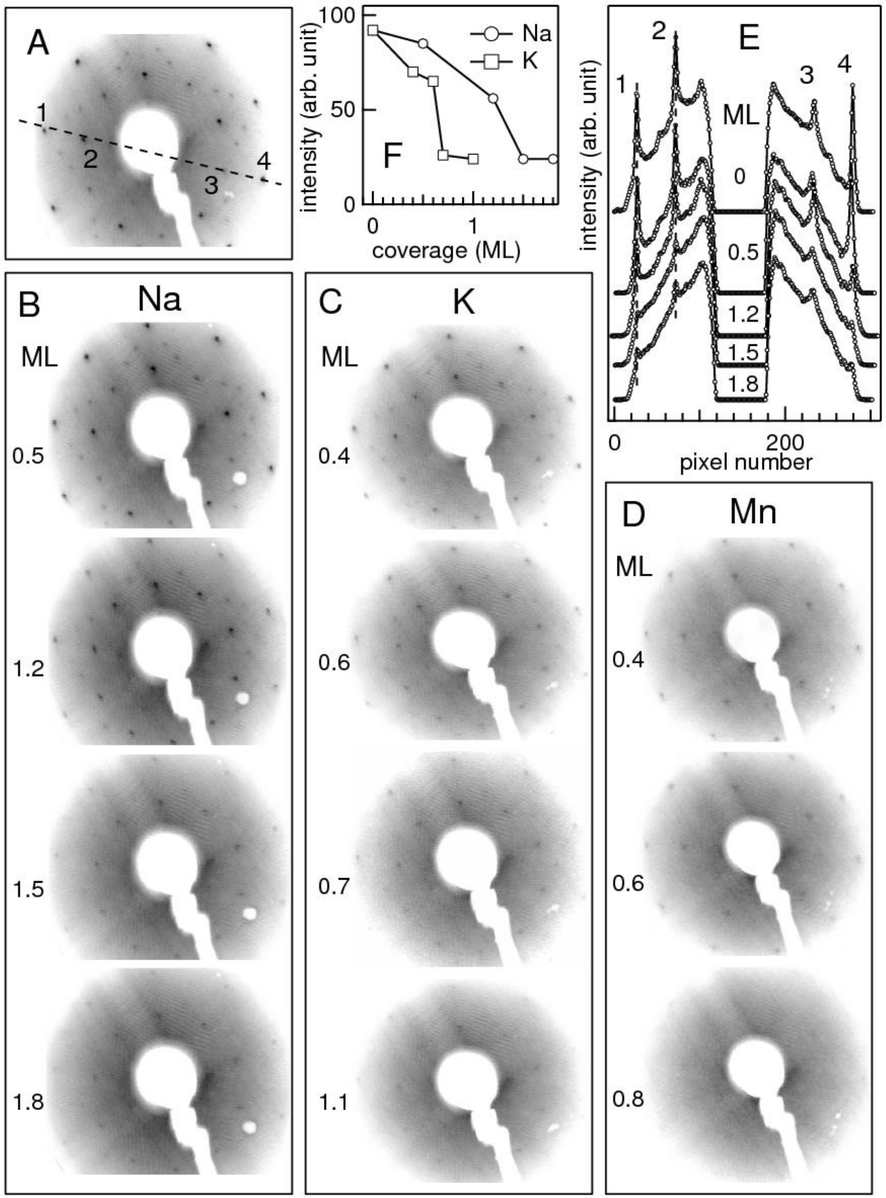
Na and K both form highly regular quasiperiodic monolayer.

Adsorption sites are mainly at the vertices of DHBS tiling.

Quasiperiodicity can propagate to the bilayer.

Na: yellow; Al: white, Pd: purple, Mn: red

Direct evidence of quasicrystallinity in Na and K adlayer



Na:

Perfect Quasiperiodicity up to 1.2 ML

Quasiperiodic order decreases for > 1.2 ML

Quasiperiodicity propagates to Na bilayer.

K:

Quasiperiodic growth up to 0.6 ML

Quasiperiodic order diminishes > 0.6 ML.

Mn:

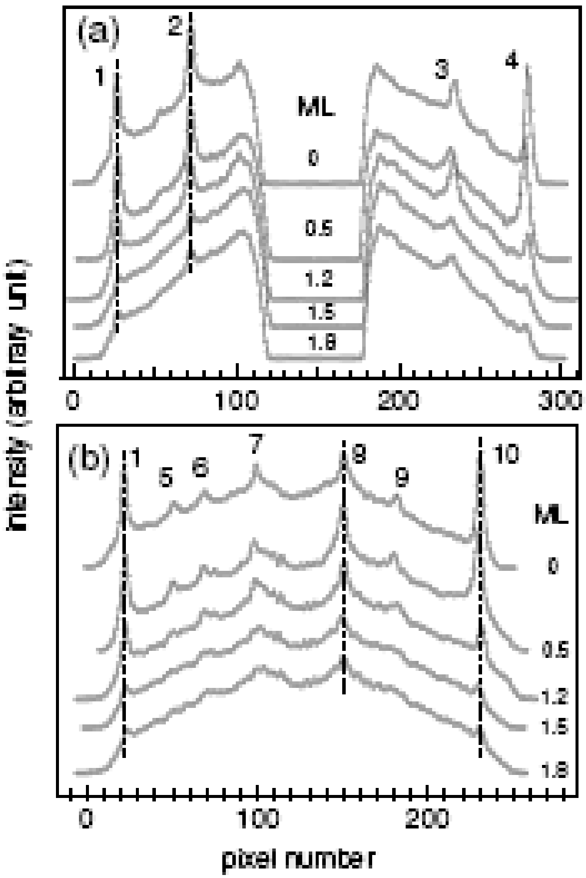
Quasiperiodic order vanishes by 0.8 ML

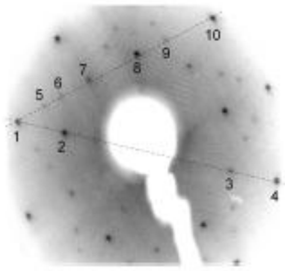
Shukla, Dhaka, D'Souza1, Maniraj, Barman, Horn, Ebert, Urban, Wu and Lograsso, J. Phys. Condensed. Matter, 21,405005 (2009).

Beam energy: 78 eV =>surface sensitive

Shukla ,Dhaka,D'Souza,Singh,Wu,Lograsso,Krajci,Hafner,Horn, and Barman, Phys. Rev. B, 79, 13406 (2009).

Intensity profiles of LEED spots as a function of Na coverage





LEED pattern of Clean i-Al-Pd-Mn at 78 eV beam energy

Spot positions are unchanged after alkali metal growth.

Quasiperiodic order is maintained.

Splitting or significant broadening of LEED spots is absent.

Adlayers are quite smooth.

Emergence of any extra spots: No

Excludes the possibility of different domains.

LEED patterns of 1.2 ML Na adlayer as a function of electron beam energies

Al/i-Al-Pd-Mn

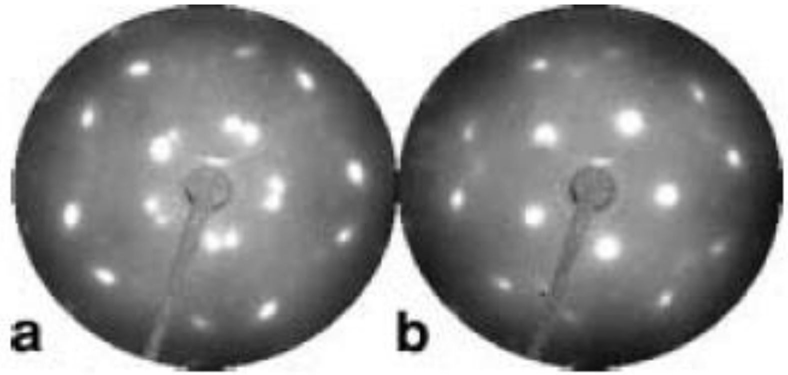
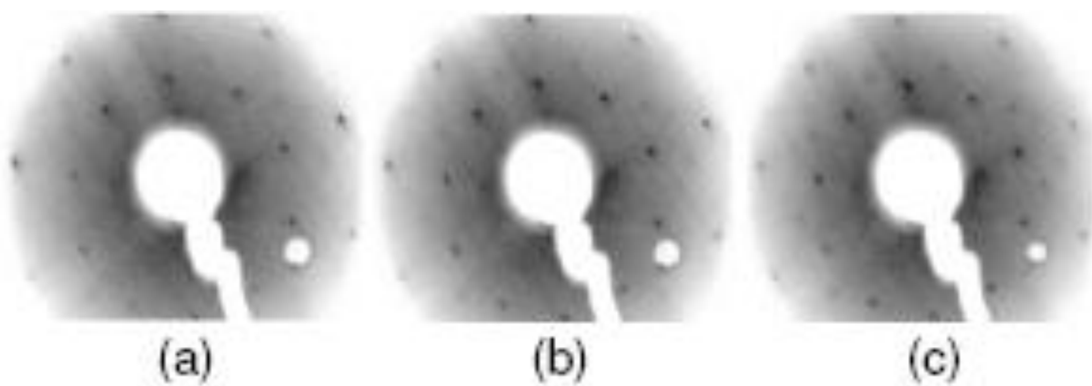


FIG. 2. LEED patterns obtained from the fivefold-symmetric surface of $Al_{70}Pd_{20}Mn_{10}$ *i*-QC at primary-electron energies of (a) 63 eV and (b) 66 eV, after evaporating a 20-Å-thick layer of Al. The fivefold symmetry of the patterns is consistent with a growth mode of Al in domains with five different orientations.

PHYSICAL REVIEW B, VOLUME 63, 052203

Na/i-Al-Pd-Mn

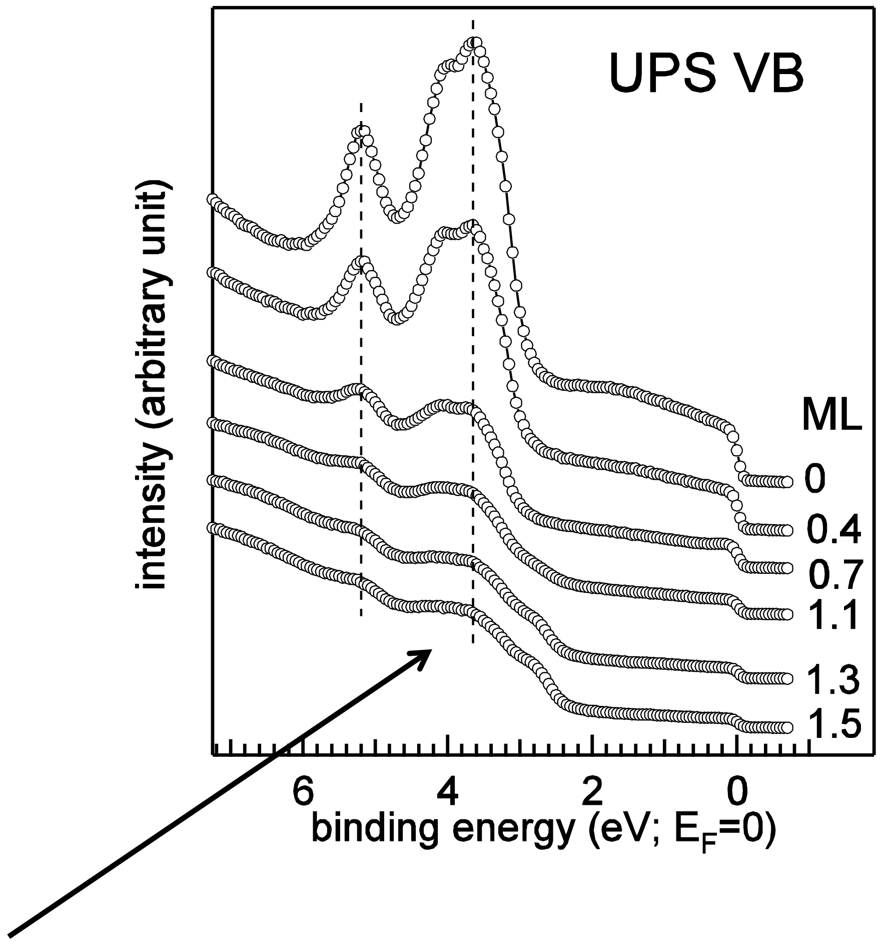
72 eV 76 eV 80 eV



No formation of twinned nano-crystallites or cubic domains.

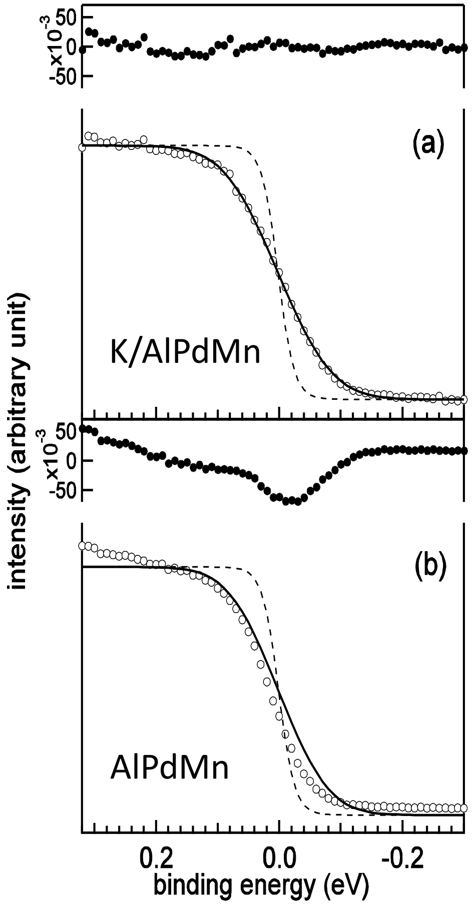
Valence band of K/i-Al-Pd-Mn

Is the pseudogap in the electronic DOS of the substrate also imprinted upon the 2D adlayer?

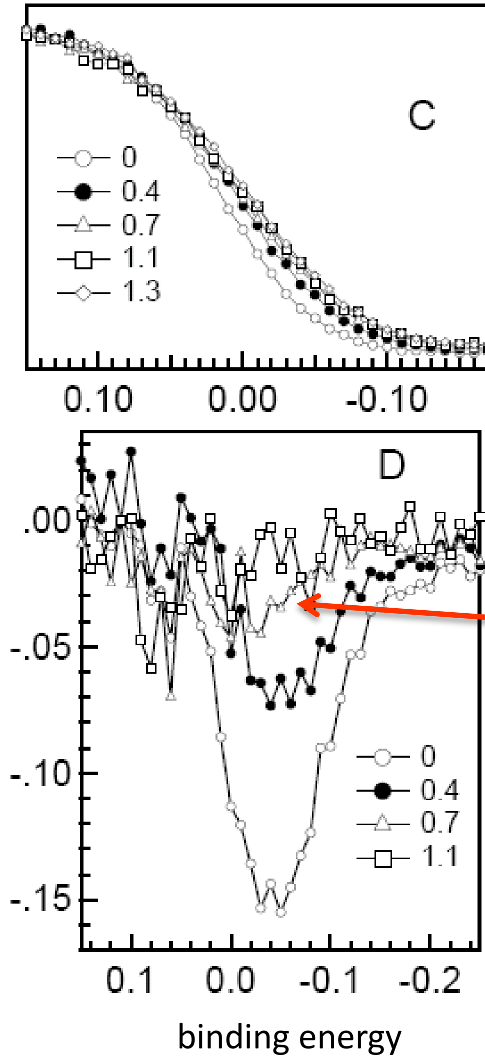


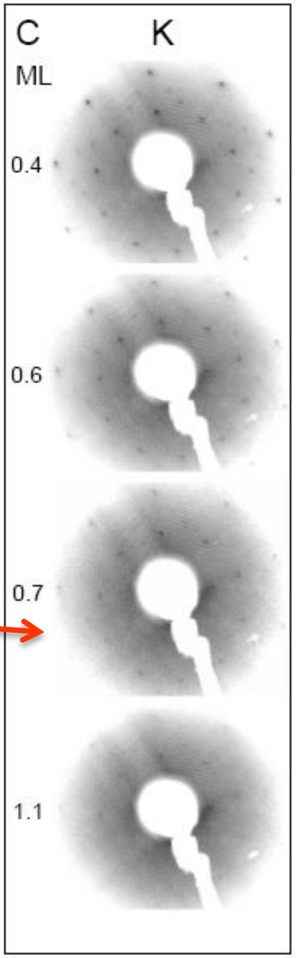
Intensity of substrate related features decreases continuously with increasing K coverage.

Pseudogap in K adlayer absent? !!



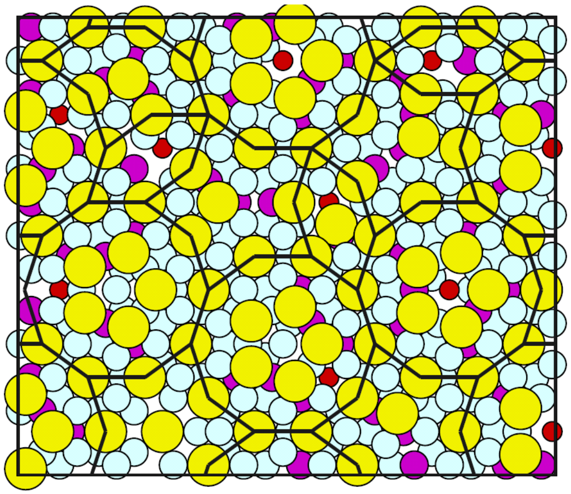
Near E_F region (open circles) of (a) 1.3 ML K coverage on i-Al-Pd-Mn, and (b) clean i-Al-Pd-Mn. Fitted curve (thick solid line) and Fermi function (dashed line) are also shown. Residual of fitting is shown at the top of each spectra.

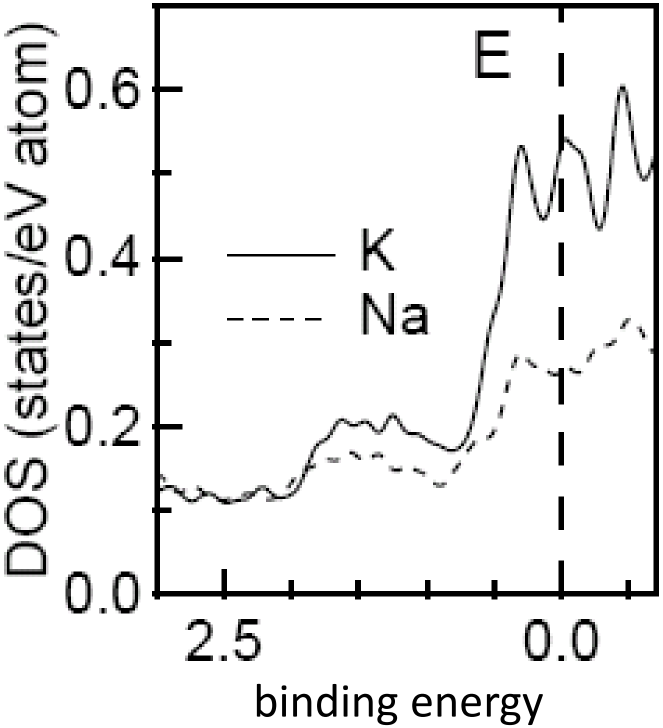




Pseudogap is not observed for quasicrystallline K layer.

Na and K adlayer DOS near E_F from ab initio theory





Pseudogap absent.

Rather a continuosly increasing DOS towards E_F : contribution of K 4s states

Stabilization of the quasiperiodic structure is the first monolayer by the strong binding of the adatoms in surface charge-density minima.

Atoms in the second monolayer are also adsorbed in hollow sites of the first layer, binding between the alkali atoms weaker

The quasiperiodic order is gradually lost in the multilayers.

Shukla , Dhaka, D'Souza, Singh, Wu, Lograsso, Krajci, Hafner, Horn, and Barman, Phys. Rev. B, 79, 13406 (2009).

Conclusions

Quasicrystalline single component metallic adlayers formed both by alkali metals on i-Al-Pd-Mn.

For Na, quasiperiodicity propagates up to the second layer.

Quasicrystallinity induced by the strong binding of the adatoms in Al-Pd-Mn surface charge-density minima. It is thus retained even in absence of the pseudogap.

Quasicrystallinity not observed in Mn/i-Al-Pd-Mn.

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Thank you for your attention