High-temperature oxygen monolayer structures on W(110) revisited

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Subject of research
A single oxygen monolayer chemisorbed on W(110) surface and ordered at high temperatures.

Motivation

to understand

- the nature of the striped superstructure
- the thermal evolution of the O-monolayer

Methods *df-LEED* *IV-LEED*

Superstructures

- **„337"** - 25-A stripes along [3-37] and [-337]
- **„113"** - 30-A stripes along [1-13] and [-113]

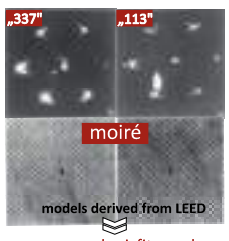
Retrospection - the milestones

1966 L. H. GERMER and J. W. MAY

at HT O-monolayer appears in TWO SUPERSTRUCTURES

discovery

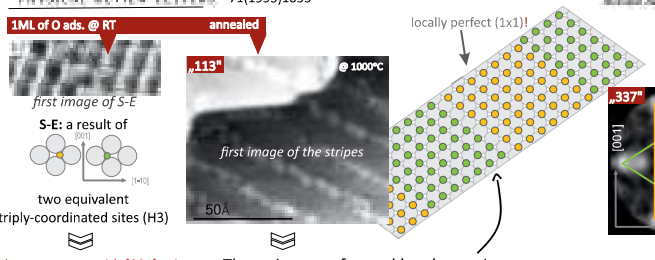
1978 E. BAUER and T. ENGEL



compressed misfit overlayer

model abandoned due to:

1993 K. E. Johnson, R. J. Wilson, S. Chiang PHYSICAL REVIEW LETTERS 71(1993)1055



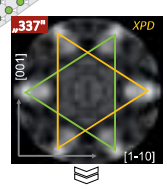
broken symmetry with [001] axis

(S-E - site exchanged domains)

„The stripes are formed by alternating S-E with locally (1x1) structure."

Johnson *et al.'s* model:

1998 H.Daimon *et al.*



. . . „113": site ?

„337": H3-like site proved

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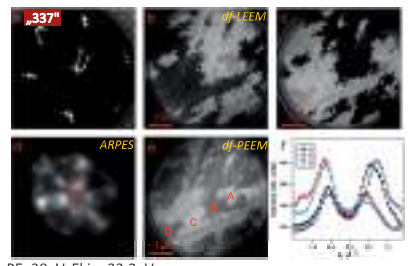
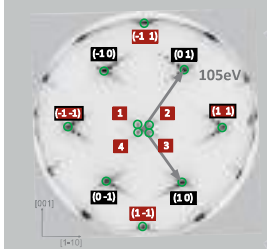


PE=38eV, Ekin=33.2eV

„337": multiply broken symmetry

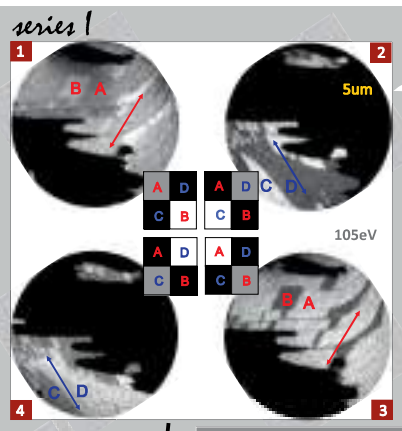
Our results

„337"



df-LEED *IV-LEED*

series I

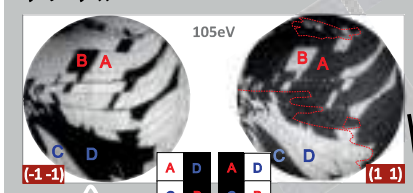


- the main contrast is due to stripes ↗ & ↘
- the sub-contrast is swapped between images acquired with the satellite spots that belong to the same rotational domain: A & B, C & D
- no correlation between main and sub-domains

In **Johnson *et al.'s* model** stripes correspond to alternating S-E (1x1) domains which break symmetry along [1-10] direction so the sub-contrast should originate from broken symetry along [001]...

Alternatively, the sublevel contrasts can be attributed to large S-E domains thus excluding the alternating ordered S-E domains to be a source of the stripes. !

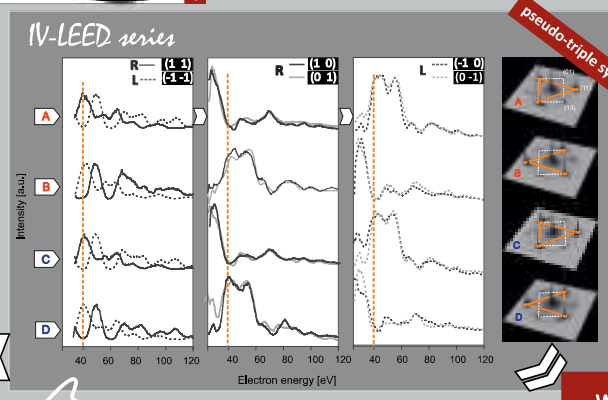
series II



- the two-level contrast perfectly reproduces the shapes of the sub-domains seen from *series I*
- A & C (B & D) with oposite stripes merge into one contrast level

sub-contrast arise from broken symmetry along [1-10] due to S-E alternating S-E stripes cannot explain this contrast !

IV-LEED series

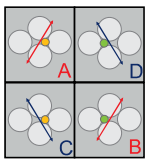


pseudo-triple symmetry

- for given sub-domain IV-LEED curves collected for specific spots on the left (L) and right (R) side of LEED pattern are none-equivalent
- A=C & B=D; A, C and B, D are mutually mirror reflected and reveal **pseudo-triple symmetry**

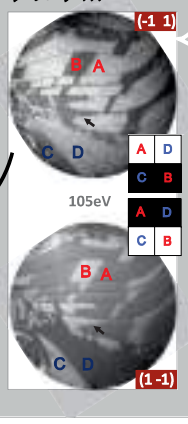
model to explain *series I, II* and IV-LEED

S-E domains and stripes are independent objects



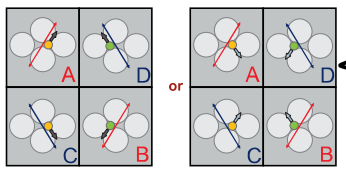
4 structures

series III



- two-level contrast suggests symmetry breaking with respect to the [1-10] axis. That is, there is an additional displacement component of the oxygen atom in the [001] direction.
- the domain boundaries are combinations of those observed in ***series I*** and ***II*** as they reflect the shapes of both the S-E domains and the rotational domains (e.g., compare the domain wall indicated with the black arrow that separates the A- and C-type domains, which belong to the same S-E domain).

modifications of the model to explain *series III*



XPD data on „337" show that oxygen atoms are additionally shifted from the ideal h3 positions in [1-10] direction outwards from the tungsten primitive cell centre thus the shift occurs probably along higher-index directions as proposed in the models above.

[001]-diplacement strictly depend on mutual relations between stripes direction and adsorption position: domains with opposite stripes and opposite sites reveal the same displacement ! !

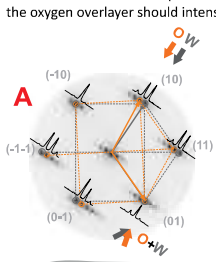
When „337" phase transforms into „113" one oxygen atoms change their adsorption site (on average) !

origin of the stripes

Johnson *et al.* model is not valid for „337" structure so misfit is an option to explain presence of the stripes. ! ...some literature data imply misfit [1, 2]

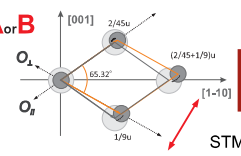
thus

we assume that LEED pattern is a result of double scattering between surface tungsten lattice and oxygen overlayer. If there is misfit between the oxygen and tungsten lattices, it would be reflected in the LEED pattern as the electrons that experience only single scattering within the oxygen overlayer should intensify specific spots with respect to the other superstructure spots.



+STM [2]

the structure



STM [2]

$G_O = \begin{bmatrix} 1 & \frac{1}{9} \\ 0 & \frac{47}{45} \end{bmatrix}$ $G_{coinc} = \begin{bmatrix} 9 & 1 \\ -2 & 5 \end{bmatrix}$

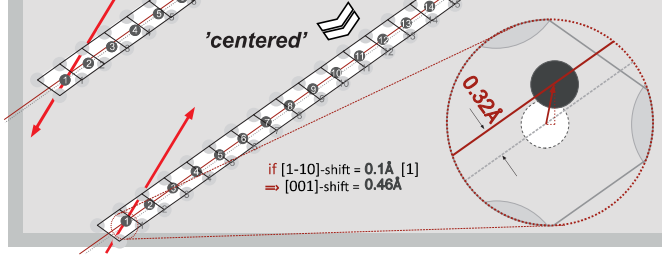
$O_{\parallel}$ is parallel to W <111>-rows
$O_{\perp}$ is not

- One close-packed O-chain ($O_{\parallel}$) runs in direction of <111> W-row.
- The other one is rotated from the corresponding <111> W- row.
- $O_{\parallel}$ is expanded in respect to W<111> counterpart
- The stripes are closer to $O_{\perp}$ and nearly perpendicular to the second close-packed O-direction, denoted as $O_{\perp}$

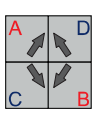
the stripes are due to expanded misfit overlayer !

Thermal evolution of oxygen overlayer undergoes via uniaxial expansion of dense-packed O-chains along <111> W-trenches !

origin of the [001]-shift



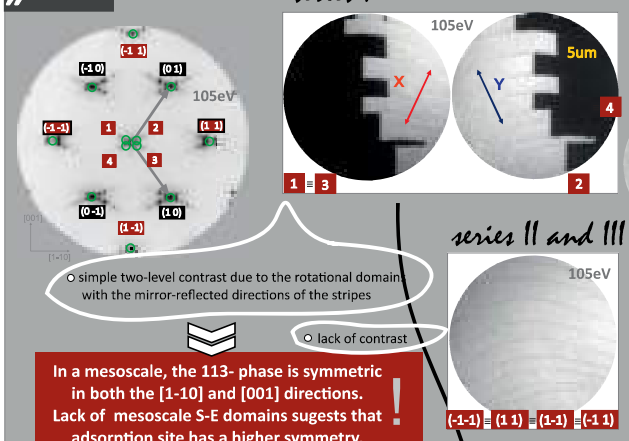
shifts for A,B, C, D domains due to 'centering':



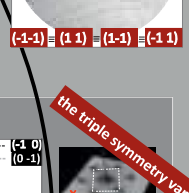
'centering' of the O-chain within the tungsten <111> - trench induces [001]-shifts (and [1-10]-ones as well) of average adsorption site accordant with contrast pattern seen in *series III* !

„113"

series I



series II and III



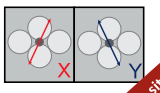
- simple two-level contrast due to the rotational domain with the mirror-reflected directions of the stripes
- lack of contrast

In a mesoscale, the 113- phase is symmetric in both the [1-10] and [001] directions. Lack of mesoscale S-E domains sugests that adsorption site has a higher symmetry. !

IV-LEED series

the triple symmetry vanishes

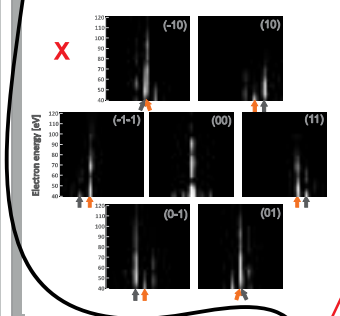
model to explain df-LEEM series and IV-LEED

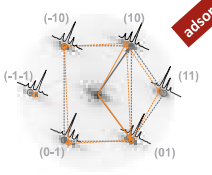


adsorption site changed !

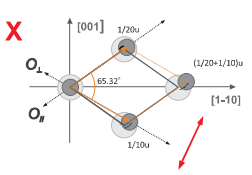
the stripes

Nature of the „113"stripes should be like for „337"





the structure

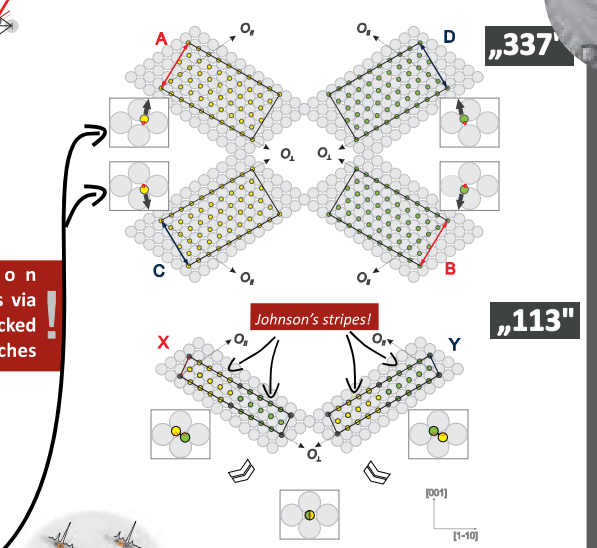


$G_O = \begin{bmatrix} 1 & \frac{1}{10} \\ 0 & \frac{21}{20} \end{bmatrix}$ $G_{coinc} = \begin{bmatrix} 10 & 1 \\ -1 & 2 \end{bmatrix}$

no [001]-shift

for such site O-chains are naturally centered along <111> W-trenches

the final models

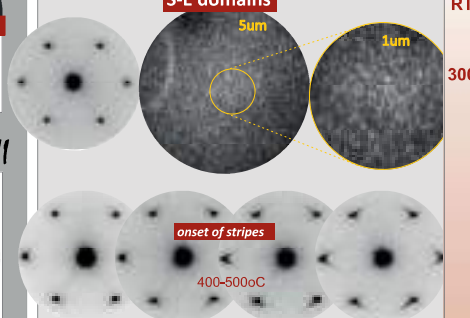


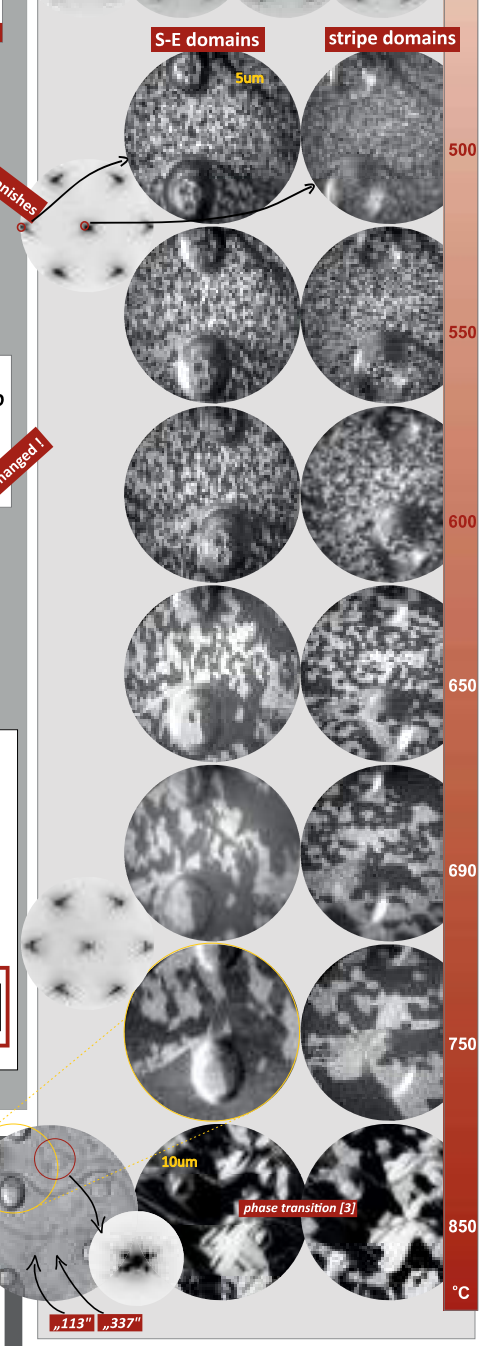
alternating S-E striped domains are present in 113 phase but they are not (1x1) and their width is half of the misfit stripes !

thermal evolution

StV=40eV

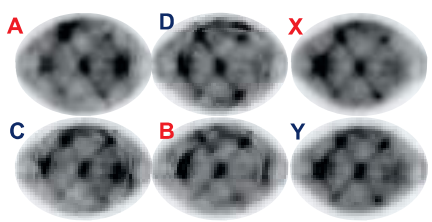
1ML O adsorbed @ 300°C





No comment

ARPES:4f 7/2 W-O
PE=80eV, Ekin=43.8eV



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Conclusions [4]

- Oxygen striped superstructures **cannot** be explained through alternating (1x1) S-E domains.
- The superstructures originate from **misfits** between tungsten and oxygen lattices.
- 113- and 337-phases **differ** in the average adsorption sites of oxygen atoms.
- Thermal evolution of oxygen monolayer occurs **via uniaxial reorganization** of close-packed chains centred along <111> W-trenches.

[1] H. Takagi, H. Daimon, F.J. Palomares, C.S. Fadley, **Surf. Sci.** 470 (2001) 189
[2] K. Radican, S.I. Bozhko, S.R. Vadapoo, S. Ulucan, H.C. Wu, A. McCoy, I.V. Shvets, **Surf. Sci.** 604 (2010) 1548
[3] T. Giela, D. Wilgocka-Ślęzak, M. Ślęzak, N. Spiridis, J. Korecki, **Appl. Surf. Sci.** 425 (2017) 314
[4] D. Wilgocka-Ślęzak, T. Giela, K. Freindl, N. Spiridis, J. Korecki, **Appl. Surf. Sci.** 528 (2020) 146712