HOKKAIDO UNIVERSITY

Institute for Catalysis ICAT

# Ni(111)上の P の吸着構造

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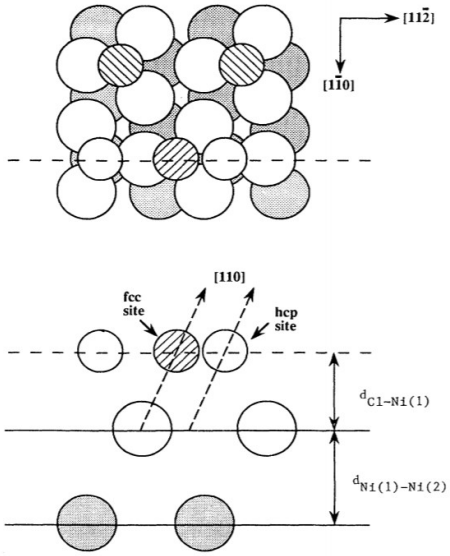
# Introduction

## Adsorption structures of Cl, S/ Ni(111)

are well established and used as a test sample for new surface analysis techniques.

Cl/Ni(111)$\sqrt{3} \times \sqrt{3}R30°$




S/Ni(111)- (2x2)

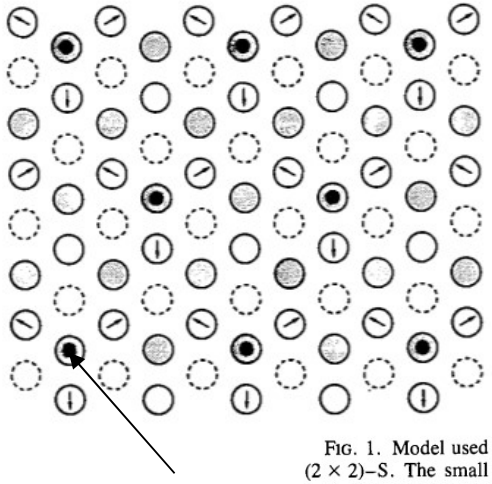
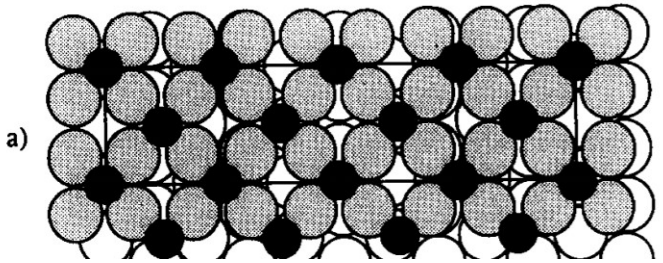



FIG. 1. Model used for the refined structural analysis of Ni(111)–(2 × 2)–S. The small filled circles represent S atoms chemisorbed in the "expected" three-fold adsorption sites; nickel atoms in the first, second, and third metal layers are represented by open circles, dashed circles, and shaded circles, respectively. The arrows define lateral displacements for nickel atoms in the first layer which correspond to positive Δ.

S/Ni(111) $(5\sqrt{3} \times 2)$

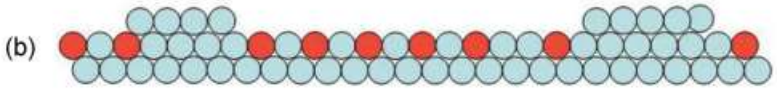



**Photoelectron diffraction**

Wang L-Q, Hussain Z, Huang Z, et al. PhysRevB. 1991;44(24):13711.

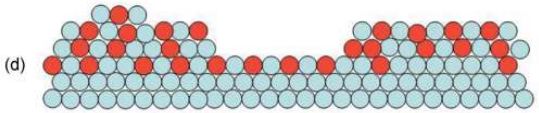
# The bonding and structure can be understood ionicity

**Cl is more ionic than S so that simple long range order by the repulsive interaction while S has more covalence so that Ni first layer reconstructed**




**Si on Ni(111)**

**2D or 3D Ni silicide is formed.**

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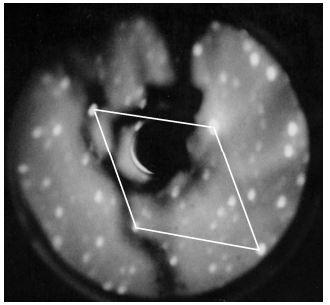
**How about P?**

**P / Ni(111) shows complicated structure**



$\sqrt{7} \times \sqrt{7}R19.1\,^{\circ}$ **and related. → Since 1999 no more work. (**Surface and Interface Analysis. 1999;28:84-91.

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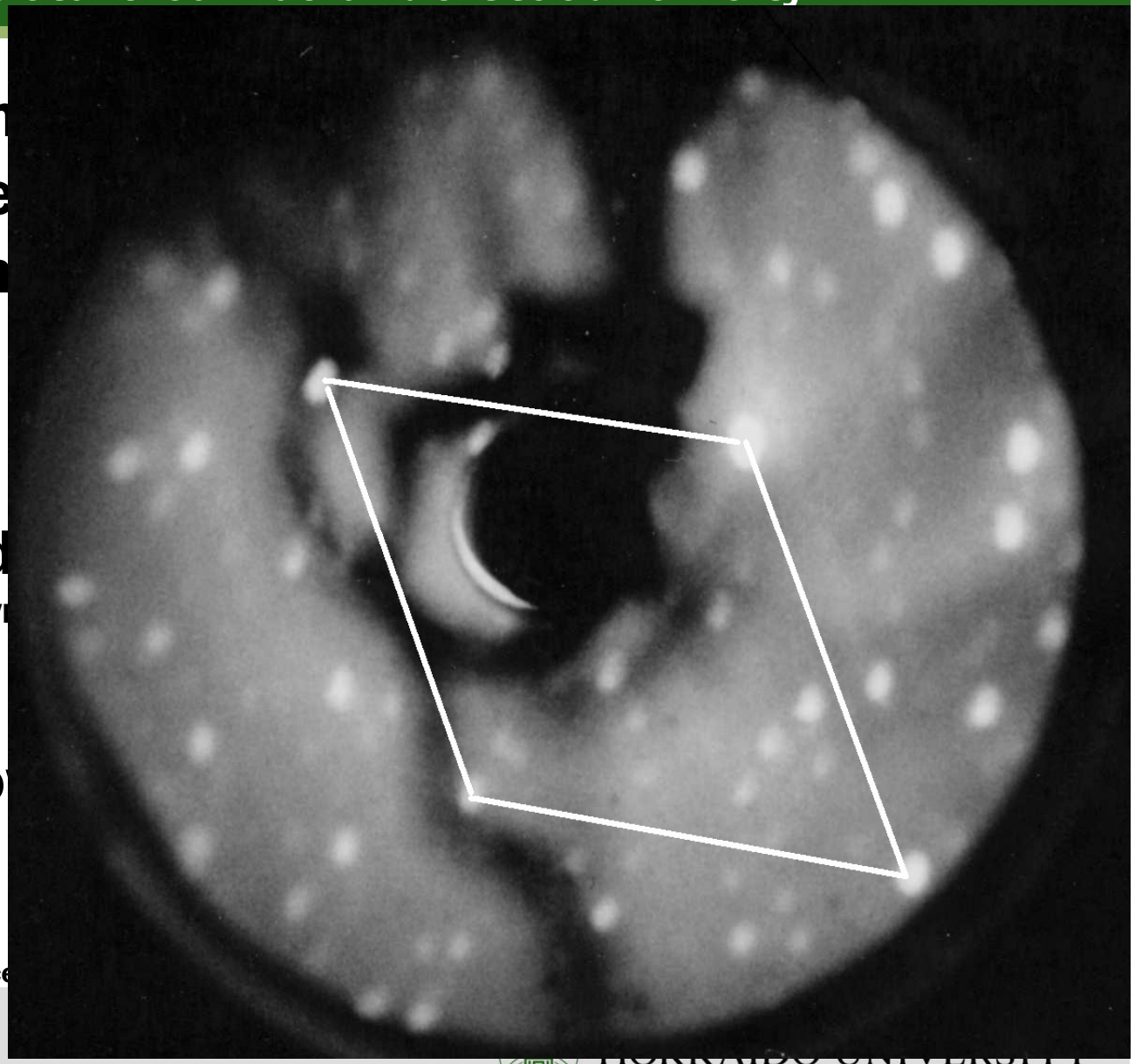

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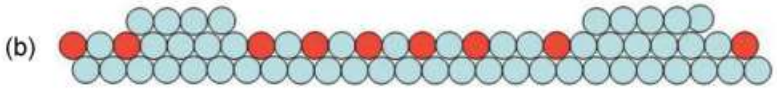


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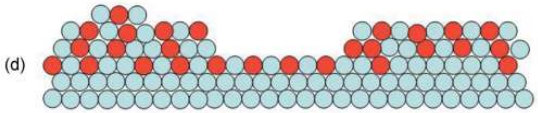


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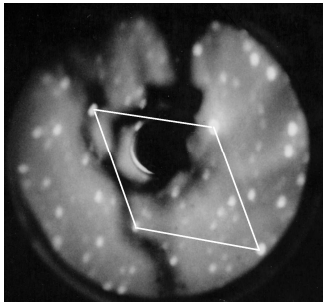

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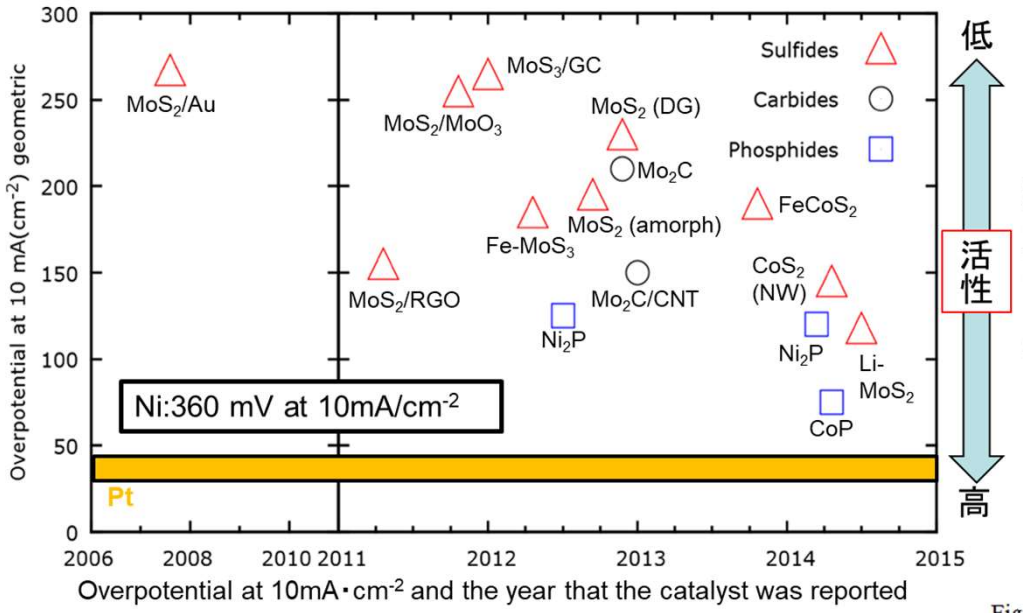
# $Ni_2P$ catalysts for HDS,HDN, HDO, HER






**Overpotential at 10mA·cm$^{-2}$ and the year that the catalyst was reported**

S. T. Oyama, *J. Catal.* 216(2003)343.

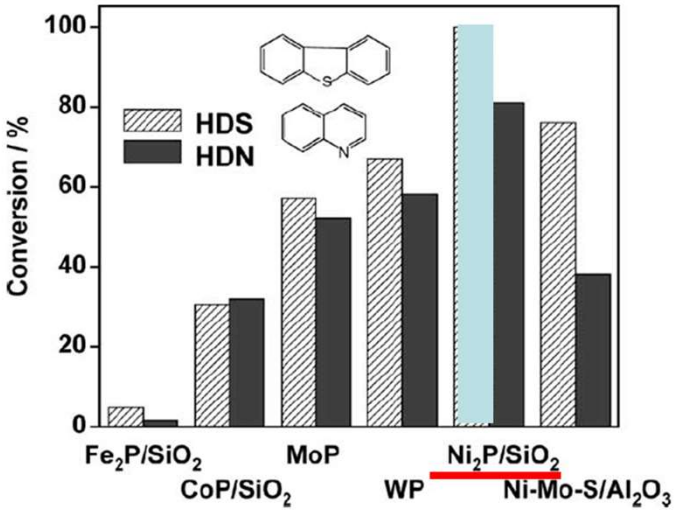
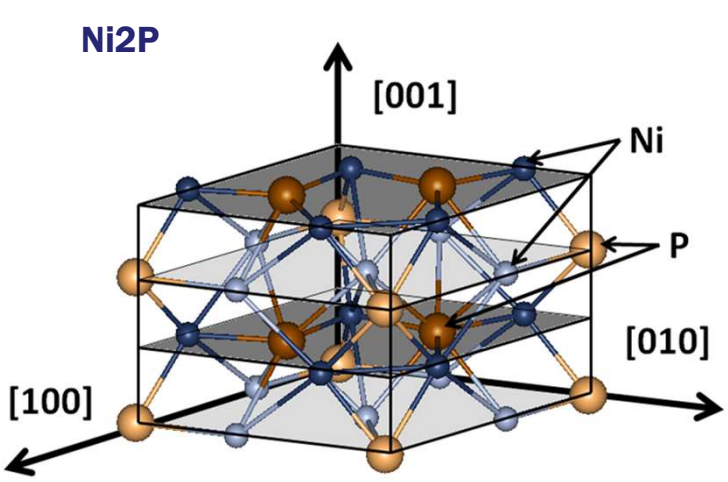
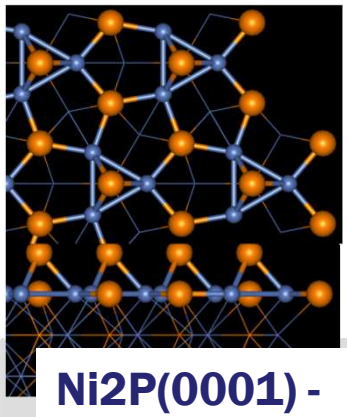
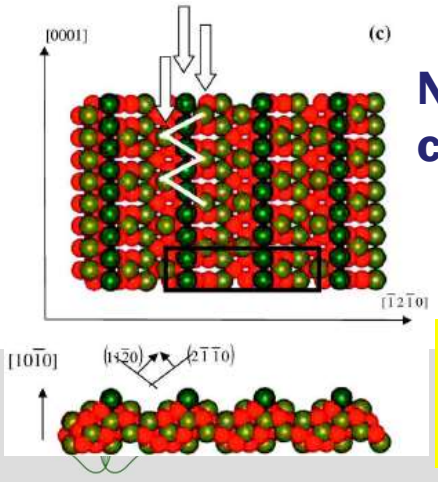



Fig. 6. Comparison of different phosphides in the hydroprocessing of a model feed. $T = 643$ K (370 °C) and $P = 3.1$ MPa (450 psig); liquid feed $= 5$ cm$^3$ h$^{-1}$; gas flow $= 150$ cm$^3$ (NTP) min$^{-1}$; bed volume $= 1$ cm$^3$.



**Ni2P(0001) - (1x1)**




**Ni2P(101b0)-c-(2x4)**

**P rich surface**

## Aim and purpose

**Revisit of P/Ni(111) adsorption structure by LEED.**

**Make a phase diagram.**

**Proposal for a new reconstruction.**

# Experimental

Ni(111) was cleaned at Ar sputtering and annealing at 873 K under about 5 × $10^{-8}$ Pa

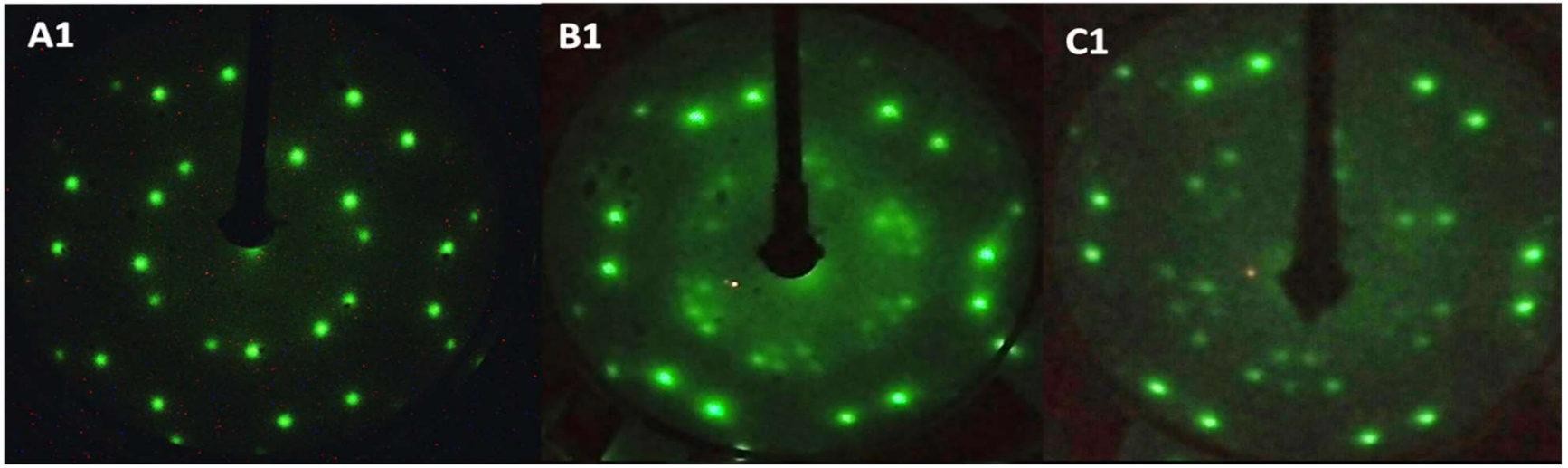
P deposition---- Decomposition of GaP

After deposition of P then anneal.

P coverage AES

Structure by LEED

# LEED patterns.




***Photographs of post anneal LEED images of P dosed onto the Ni(111) surface. Three typical patterns were obtained***

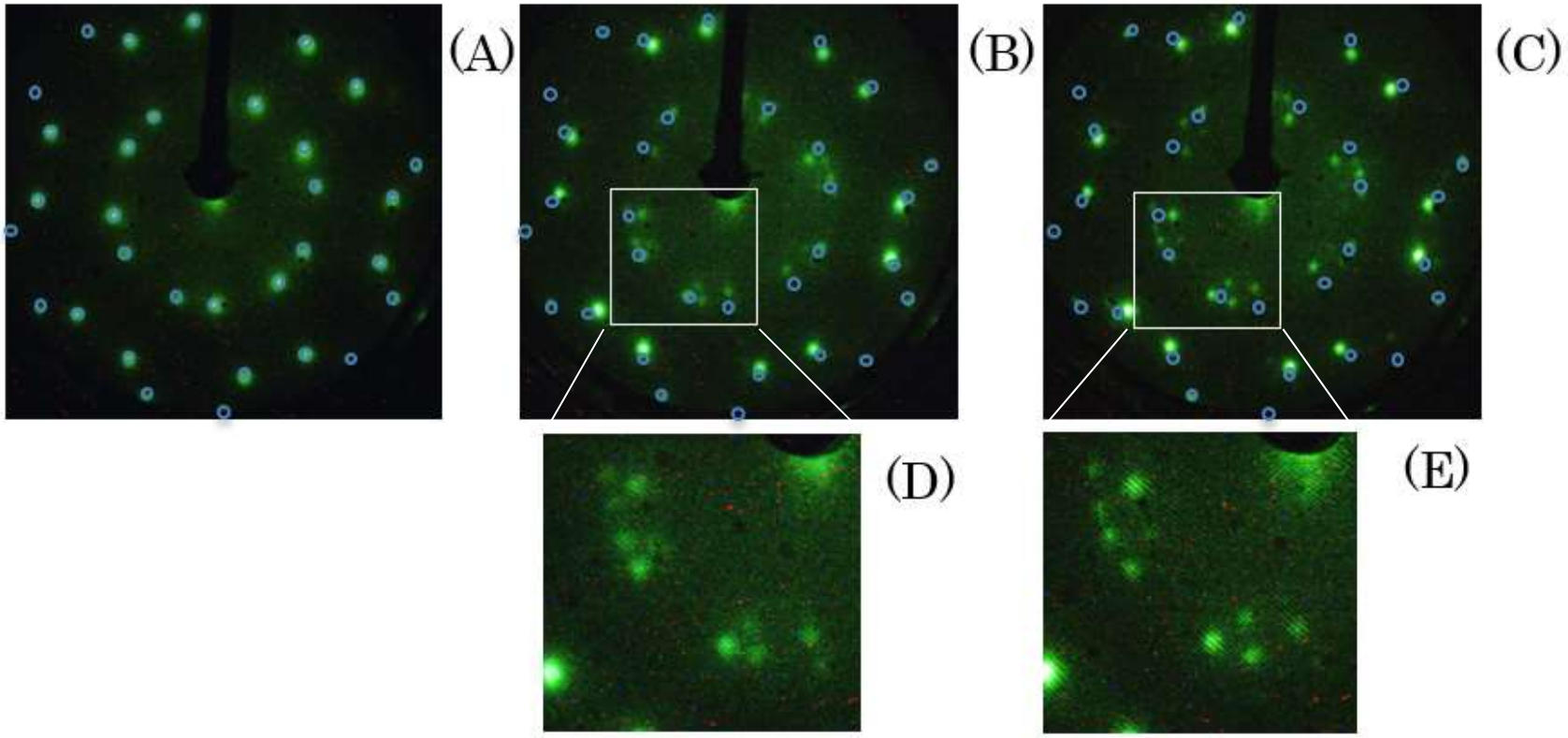
***pattern A( E=40 eV) (Coverage was 0.25 ML and annealing temperature was 373 K)*** $\sqrt{7} \times \sqrt{7}R19.1\,^{\circ}$

***pattern B(E= 40 eV ) (Coverage was 0.15 ML and annealing temperature was 873 K for less than 30 s )***

***C(E=32 eV)(Coverage was 0.12 ML and annealing temperature was 873 K for 10 min).***

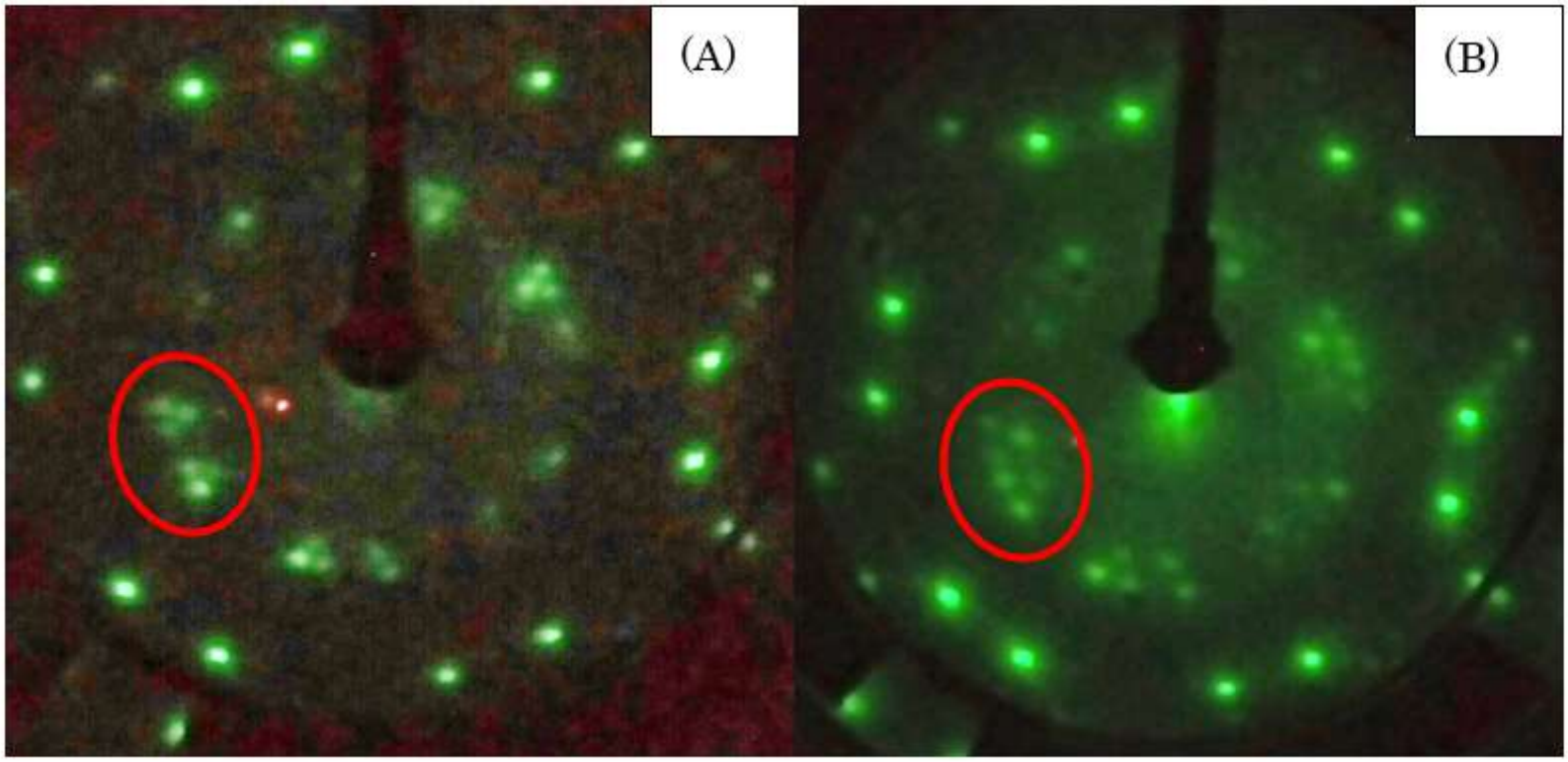
# Sequential heating

573 K for 10 min ⇨ After sequential annealing at 773 K for 10 min ⇨ After further annealing at 773 K for 10 min




**Pattern A ⟶ Pattern B ⟶ Pattern B’**

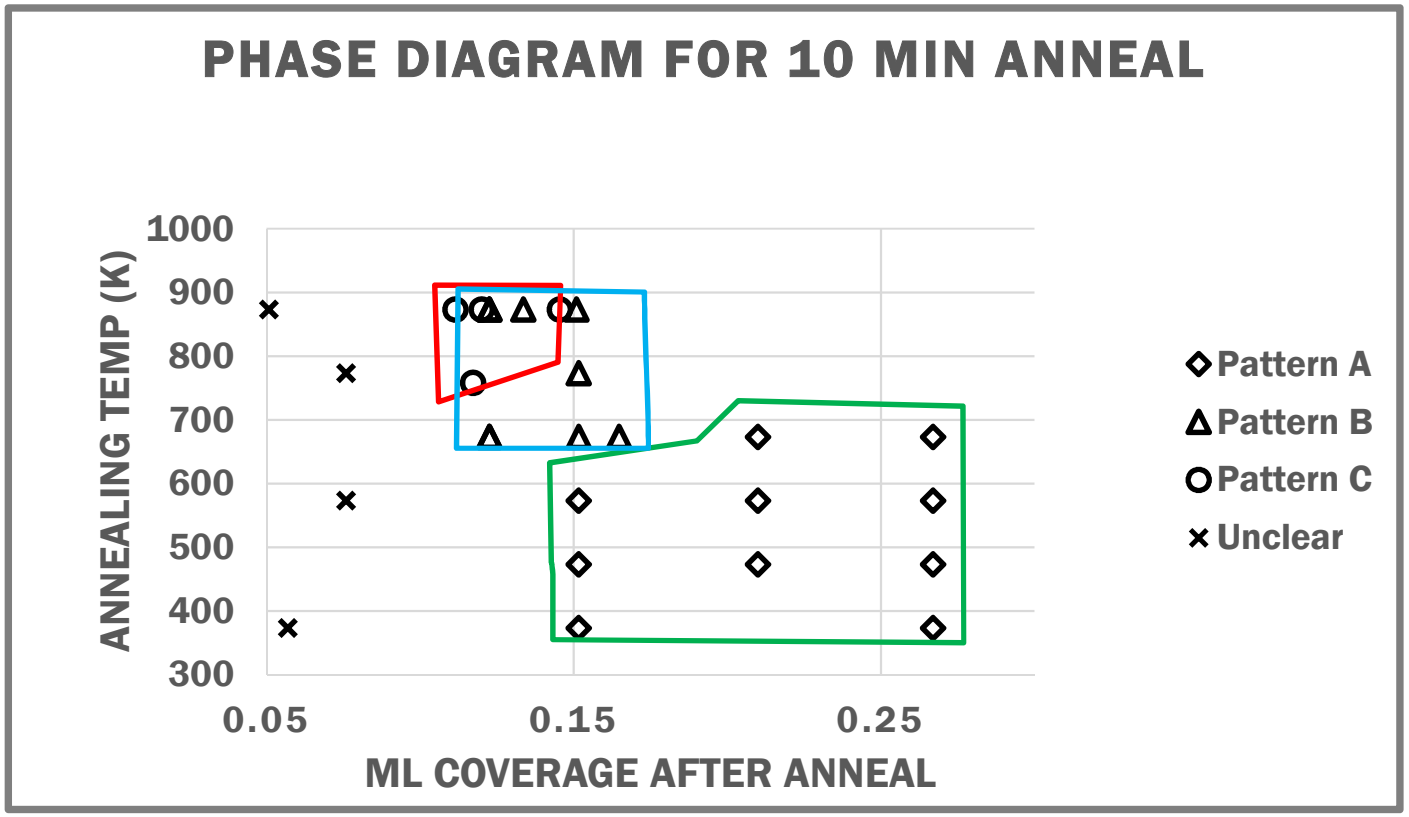
# Various Pattern B




(A) The image on the left was obtained with a 10 min annealing at 773K. (B) The image formed after an additional 10 minutes annealing.

**Pattern B is transient state to Pattern C**

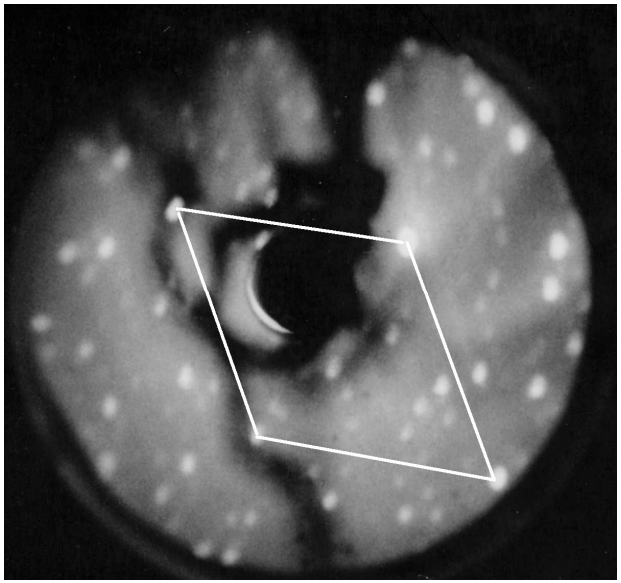
# Phase diagram.



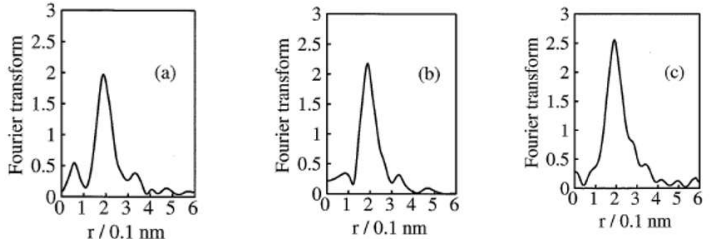

**Annealing makes the decreases of P amount**

# Lattice must be similar between 3 patterns.

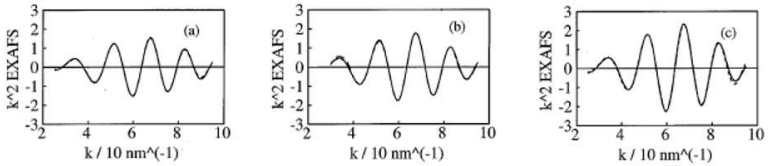
## In a previous paper



Asakura K, Konishi S, Ohta T, et al. EXAFS Studies on the Adsorption Strucutres of P/Ni(111). JpnJAppl Phys. 1993;32-2:359-61.




*ϑ=30(a), 45(b), and 90(c).*




**Rectangular surface reconstruction**

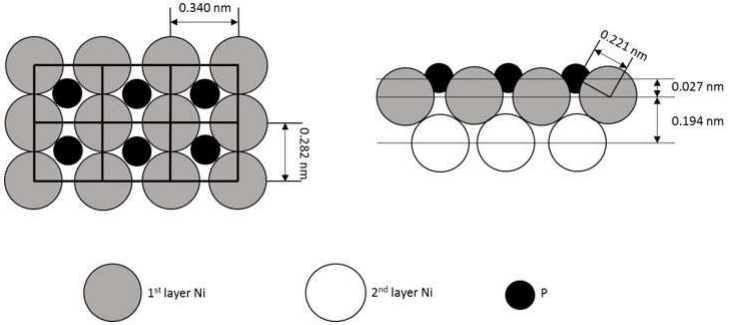
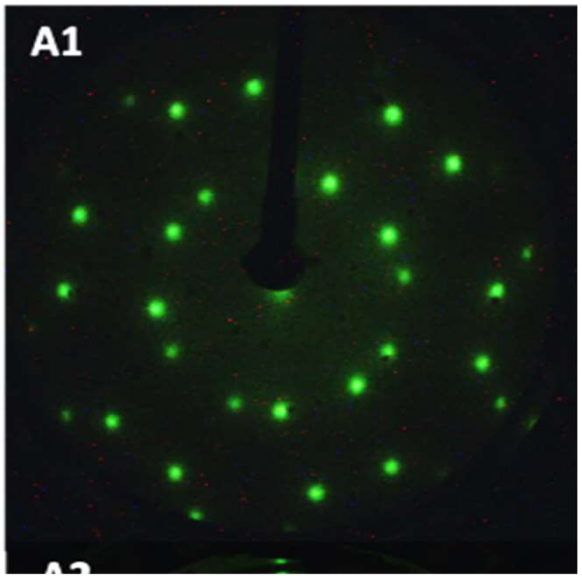
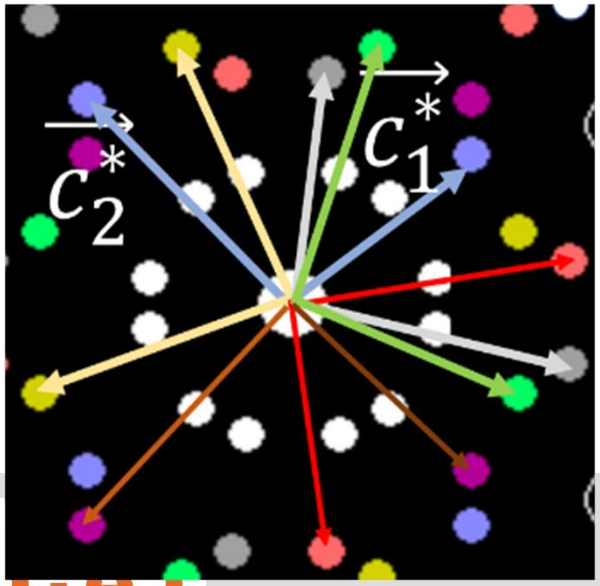


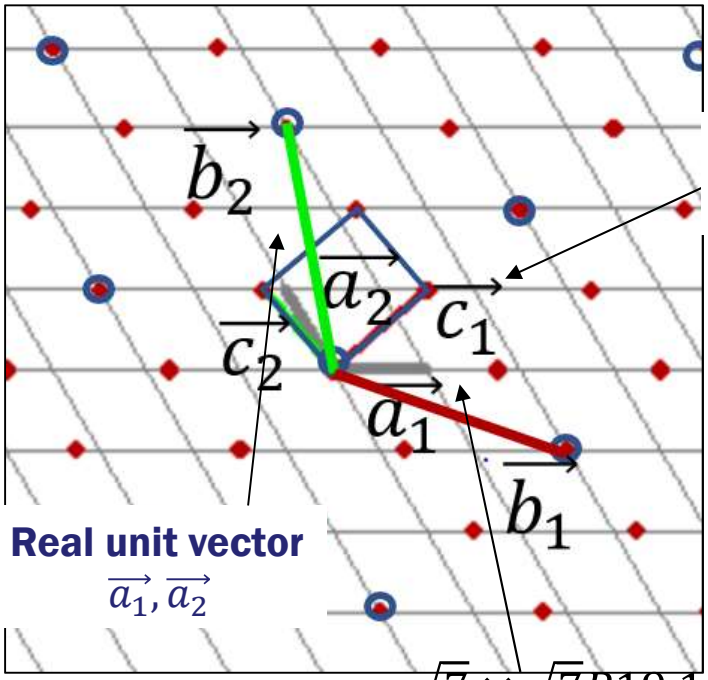

*Figure 9 Structure model for P adsorbed on reconstructed Ni surface*

# Rectangular unit cell fits the P/Ni(111) $\sqrt{7} \times \sqrt{7}R19.1°$



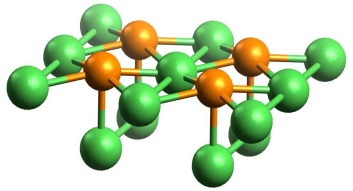



**Real unit vector**
$\overrightarrow{a_1}, \overrightarrow{a_2}$

**Rectangular unit vector**
$\overrightarrow{c_1}, \overrightarrow{c_2}$



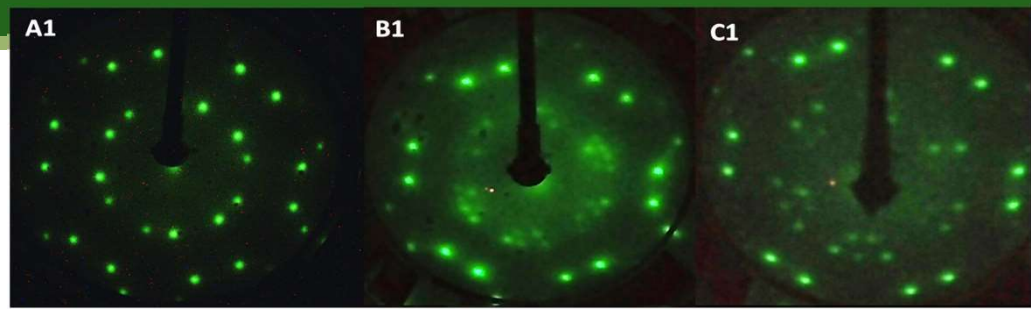
$\sqrt{7} \times \sqrt{7}R19.1°$
$\overrightarrow{b_1}, \overrightarrow{b_2}$

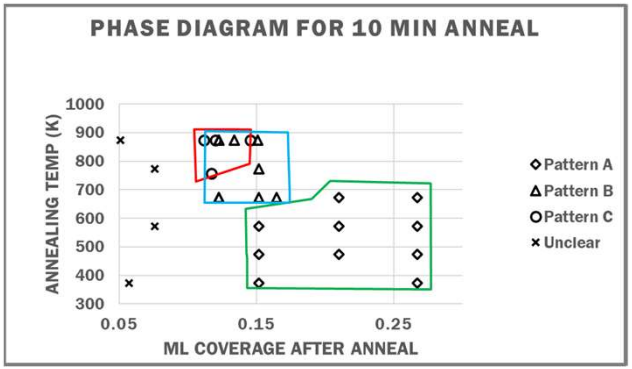
*Relations between unit vectors*

$$\begin{pmatrix} \vec{b}_1 \\ \vec{b}_2 \end{pmatrix} = \begin{pmatrix} 1 & -2 \\ 1 & 2 \end{pmatrix} \begin{pmatrix} \vec{c}_1 \\ \vec{c}_2 \end{pmatrix} \begin{pmatrix} \vec{c}_1 \\ \vec{c}_2 \end{pmatrix} = \begin{pmatrix} 1.5 & 1 \\ -0.25 & 1 \end{pmatrix} \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \end{pmatrix}$$

# Conclusions

1. Reconstructed structure of P on Ni(111) was reinvestigated.
2. Phase diagram was determined
3. Three reconstructed patterns were found.
4. Pattern B was transition state to A to C
5. Rectangular unit cell for reconstructed structure was proposed,



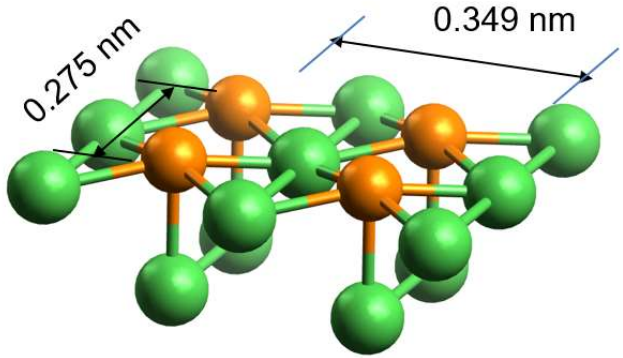




*Figure 6 Model structure proposed for the pattern C. [26] Big blue sphere is Ni and green is P.*

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# Acknowledgements

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We used several open software LEEDPat provided by FHI( http://www.fhi-berlin.mpg.de/KHsoftware/LEEDpat/ ).