A New Interpretation of the $\sqrt{7}\times\sqrt{7} r19.1^\circ$ Structure for P Adsorbed on a Ni(111) Surface

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A new interpretation of the $\sqrt{7}\times\sqrt{7}$ R19.1° structure for P adsorbed on a Ni(111) surface

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ABSTRACT
We have studied P adsorption on Ni(111), a system which shows complex adsorbate structures. We determined the phase diagram of the surface P adsorbed on Ni(111). At low coverage, amorphous P was observed. At temperatures between 373 and 673 K and coverages above 0.1 monolayer, we found a $\sqrt{7}\times\sqrt{7}$ R19.1° structure, but above 673 K, other complex structures were created. These structures seemed to correlate with each other and we reinterpret a $\sqrt{7}\times\sqrt{7}$ R19.1° structure of P adsorbed on Ni(111) based on the similarities of these surface structures. The new rectangular structure for the $\sqrt{7}\times\sqrt{7}$ R19.1° is discussed in relation to the Ni,P local structure.

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Introduction
Adsorption structures and surface reconstructions are classic topics studied in surface science [1,2]. The adsorption structures of S and Cl, for example, on Ni(111) have been well studied with various techniques. The adsorption of Cl on Ni(111) gives a $\sqrt{3}\times\sqrt{3}$ R30° pattern where Cl is adsorbed at a hollow site with no Ni below in the second layer (which is called as ‘the fcc hollow site’), and the Ni–Cl distance is 0.233 nm [3–6]. When S is adsorbed on Ni(111) at room temperature or below, $\sqrt{3}\times\sqrt{3}$ R30° overlayer structures were observed [7–13]. Complex low-energy electron diffraction (LEED) patterns, such as $5\sqrt{3}\times2$, were produced when the S/Ni(111) surface was heated [8,14–24].

In contrast to the adsorption of Cl and S on Ni(111), the adsorption structure of P on Ni(111) has rarely been reported, probably due to the observed amorphous or complex structures. When P is adsorbed on Ni(111) at room temperature, an increasing coverage causes the Ni (1×1) LEED pattern to gradually diminish without the formation of a distinct structured overlayer [25]. Two previous studies of P/Ni(111) reported clear LEED patterns after annealing the P/Ni(111). A Ni(111)-$\sqrt{7}\times\sqrt{7}$ R19.1°-P (denoted as $\sqrt{7}\times\sqrt{7}$ R19.1° P/Ni(111)) LEED pattern was obtained when the 3/7 monolayer (ML) P-covered surface was annealed to 773 K with the heating stopped as soon as 773 K was reached [26]. A more complex LEED pattern was reported by annealing a 0.15 ML P/Ni(111) to...
873 K and maintaining that temperature for 5 min [25]. These reconstructed structures were very complicated, and further studies of these structures have not been reported in the literature as far as the authors know.

Recently, Ni$_3$P, an intermetallic compound, has drawn wide interest due to its high catalytic activity. Its crystal structure belongs to the P6$_2$m space group with $a = b = 5.859$ Å and $c = 3.382$ Å [27]. The Ni$_3$P is widely used for hydrosulfurization [28] and hydrodenitrogenation [28–30] for fossil fuels, hydrodeoxygenation [31–34] for biomass conversion, and as a cathode catalyst in hydrogen evolution reactions [35,36]. The Ni$_3$P can be regarded as a substitutional material for noble metals, such as Pt and Pd. Operando X-ray absorption fine structure (XAFS) studies have revealed the reaction mechanism of hydrosulfurization, but the structure-activity relationship is not yet clear [37–40]. Surface science studies on a well-defined surface may provide more details about the structures and their relationships with catalytic activity. Several studies have been reported for Ni$_3$P single crystal surfaces [24,41–51]. X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), angle resolved photoelectron spectroscopy (ARUPS), LEED and thermal desorption spectroscopy (TDS) have all been applied to Ni$_3$P(0001) and Ni$_3$P(1010) surfaces. The surface structures of Ni$_3$P single crystals were complicated even for a (1 × 1) structure, and more complicated surfaces were observed after annealing treatments [47,52]. We have reported that P enrichment occurred to remove the Ni dangling bonds [43,53]. Control of the P concentration on the surface, however, is difficult because P atoms are always supplied from the bulk [54]. In order to better understand the Ni$_3$P catalysts, we carried out experiments on Ni(111)-P surfaces where the P was supplied by dosing from the gas-phase. Since the P supply was limited to surface deposition, P migration from the bulk could be neglected. In this work, we studied the structures of P adsorbed on Ni(111). Previously, the $\sqrt{7} \times \sqrt{7} R19.1^\circ$ structure and the more complicated structure (called pattern C in this paper) were reported independently, though the two structures showed similarities. We synthesized the two structures and obtained a comprehensive phase diagram. We also reported a new, complicated LEED pattern (called pattern B), which was previously not reported. In order to interpret these three structures consistently, we propose the rectangular surface unit cell and a new model structure for $\sqrt{7} \times \sqrt{7} R19.1^\circ$.

**Experimental details**

The experiment was carried out in two ultrahigh vacuum (UHV) chambers (about $5 \times 10^{-8}$ Pa) composed of a main chamber and a P-evaporation chamber, which were separated by a gate valve. In the main chamber, the Ni(111) single crystal was attached to a molybdenum plate and mounted on an xyzθ manipulator. The manipulator was equipped with a resistive heater and cooled with liquid N$_2$. The temperature was monitored using a thermocouple spot-welded to the side of the Ni single crystal. The Ni(111) was cleaned in the main chamber by repeated cycles of Ar ion sputtering at 2 kV for 20 min, followed by annealing at 873 K for 10 min. Cleanliness of the surface was confirmed by both a sharp $(1 \times 1)$ LEED pattern and by the absence of detectable P$_{LVV}$ and C$_{KLL}$ peaks by Auger electron spectroscopy (AES). The evaporation chamber was equipped with an evaporation source [55–57]. The evaporation chamber and the main chamber were separated by a gate valve during the GaP preheating to remove the surface impurity just before the evaporation. After preheating the GaP, the gate valve was opened to introduce P into the main chamber. The P adsorption was carried out in the main chamber. The Ni(111) sample was heated at 373 K during the P evaporation. The amount of P on the Ni was determined by AES using P$_{LVV}$ and Ni$_{LVV}$ peak ratios. Based on hydrogen thermal desorption studies of P/Ni(111) [58], a P$_{LVV}$/Ni$_{LVV}$ ratio of 0.5 corresponds to a P coverage of 0.33 ML.

**Results**

The $(1 \times 1)$ LEED spots of the Ni(111) substrate gradually became faint with the deposition of P and completely disappeared at the P saturation coverage. Approximately 0.24 ML of P was deposited, and the surface was annealed to chosen temperatures (573–873 K); three types of LEED patterns designated as pattern A, pattern B, and pattern C were observed, as shown in Figure 1.

We deposited 0.26 ML P on Ni(111) at 373 K, we obtained Pattern A. Pattern A was consistent with a $\sqrt{7} \times \sqrt{7} R19.1^\circ$ diffraction pattern, which had previously been reported on Ni(111) [26]. Figure 2 shows a $\sqrt{7} \times \sqrt{7} R19.1^\circ$ structure drawn in LEEDPat4.2 [59] with its commonly used reciprocal lattice unit vectors. $\overrightarrow{a}_1$ and $\overrightarrow{a}_2$ were the Ni(111) surface lattice unit vectors while $\overrightarrow{b}_1$ and $\overrightarrow{b}_2$ were the overlayer lattice unit vectors. The structure was composed of two domains, which had a mirror symmetry relation with each other as shown in Figure 2. The 12 spots appeared around $(0,0)$.

Figure 1(b) shows LEED pattern B after annealing at 873 K for 30 sec. Pattern B had LEED spots that corresponded well with those of $\sqrt{7} \times \sqrt{7} R19.1^\circ$ especially around $(n,m)$ $(n$ or $m = 1, -1)$. The spots around $(0, 0)$ (on the dashed line in Figure 2(b)) were split into three spots compared to pattern A, indicating that
pattern B had a unit cell incommensurate to the substrate unit cell. These groups of three spots around (0,0) were always weak and diffuse. Consequently, 12 sets of three split spots appeared around (0,0). We believe that pattern B corresponds to a newly reported structure.

At higher temperatures that ranged from 773 and 873 K, pattern C appeared where 6 sets of 5 spots were found in the inner circle. The \( \sqrt{7} \times \sqrt{7} R19.1^{\circ} \) spots were stronger around \((n,m)\) \((n \text{ or } m = 1,-1)\). This pattern C corresponds to the one observed previously on P on Ni(111) prepared by PH\(_3\) deposition \[25\]. Note that the coverage decreased with temperature. When the initial coverage of P was 0.24 ML, 873 K annealing produced pattern C and reduced the P coverage to 0.12 ML, probably due to the diffusion into bulk Ni or evaporation from the surface.

Figure 1. Photographs of LEED images of post annealed surfaces of P dosed onto the Ni(111) surface. a1, a2: pattern A which was formed after 0.26 ML P was deposited on Ni(111) heated at 373 K. b1, b2: images of a series of patterns referred to as pattern B (coverage was 0.15 ML and annealing temperature was 873 K for less than 30 s). c1, c2: pattern C (coverage was 0.12 ML and annealing temperature was 873 K for 10 min). Acceleration energies were 40 eV for a1 and b1, 32 eV for c1, respectively. Acceleration energies for a2, b2 and c2 were 80, 75 and 70 eV, respectively.

Figure 2. (a) \( \sqrt{7} \times \sqrt{7} R19.1^{\circ} \) LEED pattern with the reciprocal lattice unit vectors. Red and blue short vectors indicate different domains. Dashed and dot-dashed circles indicate the inner circle around (0,0) and the one around (0, -1), respectively. (b) the real space substrate lattice and its lattice unit vectors \((\vec{a}_1, \vec{a}_2)\). Blue and red points indicated the lattice associated with \( \sqrt{7} \times \sqrt{7} R19.1^{\circ} \) for two different domains, respectively. \( \vec{b}_1 \) and \( \vec{b}_2 \) were overlayer lattice unit vectors.
In order to see the relation between these patterns, we carried out subsequent heating. Figure 3(a) shows the $\sqrt{7} \times \sqrt{7} R19.1^\circ$ after 573 K annealing. When the sample was heated to 773 K, pattern B was observed, as shown in Figure 3(b). Figure 3(b) has blue open circles which serve as a visual guide and correspond to the $\sqrt{7} \times \sqrt{7} R19.1^\circ$ spots seen in Figure 3(a). These spots were slightly shifted in the direction of the substrate reciprocal lattice unit vector, as shown in Figure 3(b). In addition, their positions were varied with the annealing temperature and duration time as shown in Figure 3(c) where the sample was heated at 773 K for another 10 min. The difference between Figure 3(b) and (c) was the location of the three split spots. The three split spots were expanded, and two sets of the neighboring split spots moved closer to each other with increased annealing time. Pattern B appeared to be a transient structure. Further expansion of the three split spots transformed the two sets of three split spots into one set of 5 spots observed in pattern C. These similarities and continuous changes indicated that the unit cells of pattern A, pattern B and pattern C were closely related.

Figure 4 shows the phase diagram of P on Ni(111). Here, each sample was annealed at the designated temperatures. The coverages reported were measured by AES after the annealing and LEED measurements. For coverages less than 0.08 ML, we could not detect a LEED pattern since the surface remained amorphous. For coverages greater than 0.11 ML, the $\sqrt{7} \times \sqrt{7} R19.1^\circ$ structure started to appear above 373 K. If the sample was heated above 673 K, we observed pattern B where the $\sqrt{7} \times \sqrt{7} R19.1^\circ$ spots were split into three. Pattern B is a transient structure, and the spot positions gradually changed with further annealing. Finally, when the sample was annealed above 773 K–873 K, pattern C was observed. Since pattern B was a transient state from pattern A to pattern C, we had overlapping areas of pattern B and pattern C where both pattern formations were highly dependent on the dosing amount, annealing temperature, and annealing time.

**Discussion**

The $\sqrt{7} \times \sqrt{7} R19.1^\circ$ overlayer lattice unit vector $\overrightarrow{b_1}$ and $\overrightarrow{b_2}$ were expressed by the substrate vectors, $\overrightarrow{a_1}$ and $\overrightarrow{a_2}$ as

$$\overrightarrow{b_1} = 2 \overrightarrow{a_1} - \overrightarrow{a_2}$$
$$\overrightarrow{b_2} = \overrightarrow{a_1} + 3\overrightarrow{a_2}$$

Or

$$\begin{pmatrix} \overrightarrow{b_1} \\ \overrightarrow{b_2} \end{pmatrix} = \begin{pmatrix} 2 & -1 \\ 1 & 3 \end{pmatrix} \begin{pmatrix} \overrightarrow{a_1} \\ \overrightarrow{a_2} \end{pmatrix}$$

This can be graphically shown as in Figure 2. The reciprocal lattice unit vector was written as
\[
\left( \begin{array}{c}
\tilde{b}_1 \\
\tilde{b}_2
\end{array} \right) = \frac{1}{7} \left( \begin{array}{cc}
3 & -1 \\
1 & 2
\end{array} \right) \left( \begin{array}{c}
\tilde{a}_1 \\
\tilde{a}_2
\end{array} \right)
\]

Saidy et al. produced a hexagonal unit cell to explain the \(\sqrt{7} \times \sqrt{7}\) R19.1° structure [26]. In their model structure, 3 Ni atoms were replaced with 3 P atoms. The maximum coverage of P was thus 0.57 ML. However, this hexagonal unit cell could not explain the three split spots in pattern B. To observe the three split spots, the breakdown of 3 fold rotational symmetry is necessary. We could reproduce the three split spots in the inner circle around (0,0) if the angle between the overlayer lattice unit vectors \(\tilde{b}_1\) and \(\tilde{b}_2\) was set to 130° and the angle between the overlayer lattice unit vector and the substrate \((\tilde{b}_2\) and \(\tilde{a}_2\)) was set to −9.1° instead of −19.1°. As in pattern C, 6 sets of five spots could be seen by the rotation of the overlayer by 9.1° where the angle between \(\tilde{b}_2\) and \(\tilde{a}_2\) became 0°. This lattice unit vector allowed us to create the incommensurate surface structure by breaking down the three-fold rotational symmetry. Unfortunately, this approach also had a fatal problem in that there was no agreement between the calculated and observed spots around \((m,n)\) \((m\) or \(n = −1,1)\). This lack of model agreement occurred because the spots around the inner circle around the (0,0) spot were used for the reciprocal lattice unit vectors. It is not necessary to select the spots around \((0,0)\) as the reciprocal lattice unit vectors because electron diffraction suffers strongly from multiple scattering [60]. Since the spots around \((m,n)\) \((m\) or \(n = −1,1)\) appeared stronger in pattern B and pattern C, these spots could be regarded as the reciprocal lattice unit vectors. The spots around \((0,0)\) appeared as a result of multiple scattering. Based on this idea, we reinterpreted the \(\sqrt{7} \times \sqrt{7}\) R19.1° pattern. We previously proposed the structure for pattern C as shown in Figure 5 based on extended x-ray absorption fine structure (EXAFS) analysis [25], where the topmost two layers of Ni were reconstructed to a rectangular unit cell. The P was adsorbed above the center of the rectangular unit. If we reproduced the \(\sqrt{7} \times \sqrt{7}\) R19.1° based on this rectangular model, we could connect pattern A (\(\sqrt{7} \times \sqrt{7}\) R19.1°) and pattern C. After trial and error, we found the rectangular unit cell could indeed be well fit to the hexagonal \(\sqrt{7} \times \sqrt{7}\) R19.1°. First, we selected the surface reciprocal lattice vectors from the spots on the circle around \((m,n)\) \((m\) or \(n = −1,1)\) shown as \(\tilde{c}_1\) and \(\tilde{c}_2\) in Figure 6(a).

The relationship between \((\tilde{c}_1, \tilde{c}_2)\) and \((\tilde{a}_1, \tilde{a}_2)\) was

\[
\left( \begin{array}{c}
\tilde{c}_1 \\
\tilde{c}_2
\end{array} \right) = \left( \begin{array}{cc}
1.5 & 1 \\
-0.25 & 1
\end{array} \right) \left( \begin{array}{c}
\tilde{a}_1 \\
\tilde{a}_2
\end{array} \right)
\]

\(|\tilde{c}_1| = \frac{\sqrt{7}}{2} |\tilde{a}_1|, \quad |\tilde{c}_2| = -\frac{\sqrt{21}}{4} |\tilde{a}_1|
\]

\[\begin{align*}
\begin{pmatrix}
C_1 \\
C_2
\end{pmatrix} &= \begin{pmatrix}
4/7 \\
-4/7
\end{pmatrix} \begin{pmatrix}
a_1^2 \\
a_2^2
\end{pmatrix}, \\
\begin{pmatrix}
a_1 \\
a_2
\end{pmatrix} &= \begin{pmatrix}
2 & -1 \\
1 & 3
\end{pmatrix} \begin{pmatrix}
\tilde{a}_1 \\
\tilde{a}_2
\end{pmatrix}
\end{align*}\]

The \((\tilde{b}_1, \tilde{b}_2)\) required for the \(\sqrt{7} \times \sqrt{7}\) R19.1° structure were the unit cell vectors for which both the \((\tilde{c}_1, \tilde{c}_2)\) and \((\tilde{a}_1, \tilde{a}_2)\) lattices were commensurate as shown in

\[
\left( \begin{array}{c}
\tilde{b}_1 \\
\tilde{b}_2
\end{array} \right) = \left( \begin{array}{cc}
1 & -2 \\
1 & 2
\end{array} \right) \left( \begin{array}{c}
\tilde{c}_1 \\
\tilde{c}_2
\end{array} \right) = \left( \begin{array}{cc}
2 & -1 \\
1 & 3
\end{array} \right) \left( \begin{array}{c}
\tilde{a}_1 \\
\tilde{a}_2
\end{array} \right)
\]

The spots around the \((0,0)\) appeared as the result of multiple scattering events in the overlayer and the substrate lattices that reproduced the LEED patterns as shown in Figure 6(b). For example, \((\tilde{b}_1, \tilde{b}_2)\) is created by \(-\tilde{c}_1 + \tilde{a}_1^2\) in Figure 6(b). Note that the multiple scattering spots of the other domains appeared at the same position. For example, the multiple scattering spots of \((\tilde{a}_1^2, \tilde{a}_2^2)\) in the second domain (Domain 2 of Figure 6(c)) and of \((\tilde{c}_1, \tilde{c}_2)\) in the third domain (Domain 3 of Figure 6(c)) gave the same spot. In other words, the spots around the \((0,0)\) were triply degenerated spots. This meant when the rectangular unit vectors were slightly deformed, these spots were split into 3 spots, corresponding to pattern B.

Thus, the rectangular unit cell and multiple scattering events can rationally explain the \(\sqrt{7} \times \sqrt{7}\) R19.1° structure and its continuous transition to patterns B and C. Moreover, the strong spots in pattern B and pattern C are understood by the reciprocal lattice unit vector, although further calculations are necessary to completely reproduce all of the spots in pattern B and pattern C.

In the literature, the \(\sqrt{7} \times \sqrt{7}\) R19.1° is usually interpreted in terms of a hexagonal overlay. In the LEED analysis of \(\sqrt{7} \times \sqrt{7}\) R19.1° of P/Ni(111), 4 surface Ni atoms out of 7 were replaced with 4 P atoms to produce the mixed overlayer of Ni and P [26]. The
overlayer for S adsorbed on Cu(111) [61,62], Rh(111) [63–65] and Pd(111) [66,67] had similar structures, maintaining the hexagonal unit cell. The rectangular lattice structure we propose is unique and explains the relationship between the \( \sqrt{7} \times \sqrt{7} \) \( R \) 19.1° structure and the two incommensurate structures of pattern B and pattern C. In the literature we found one other example of the formation of an overlayer with a different lattice system. This example was the \( \sqrt{3} \times \sqrt{3} \) pattern on Ni(111), where the surface overlayer had a square lattice [24]. S was adsorbed on the square-reconstructed Ni surface to increase the number of S-Ni bonds.

Hereinafter, we continue to discuss the possible local structure around P based on the rectangular reconstruction. We have proposed a rectangular unit cell for pattern C, as shown in Figure 5, which has dimensions 0.275 \( \times \) 0.349 nm. P adsorbs on the center of the reconstructed Ni rectangular unit. If a similar unit cell is formed in pattern A, or \( \sqrt{7} \times \sqrt{7} \) \( R \) 19.1°, the rectangular structure has size 0.284 \( \times \) 0.329 nm. In this model structure the maximum coverage of P should be 4/7 ML. This structure can be related to the local structure found in the (1120) surface of the Ni\(_2\)P crystal, which has a rectangular 0.261 \( \times \) 0.338 nm lattice. Each corner of this rectangular local structure has Ni atoms, as shown in Figure 7. P is situated at the Ni 4-fold hollow site. Therefore the rectangular unit of the \( \sqrt{7} \times \sqrt{7} \) \( R \) 19.1° structure has a similar local structure to Ni\(_2\)P.

Further reconstructions to pattern B and C might occur to produce more stable structures. Pattern B might be the transient structure from the \( \sqrt{7} \times \sqrt{7} \) \( R \) 19.1° structure to the structure of pattern C. In order to measure the actual unit cell dimension and to confirm the definite conclusions, we need further calculations and experiments on the \( \sqrt{7} \times \sqrt{7} \) \( R \) 19.1° structure of P/Ni(111) using atomic scale STM and EXAFS.

**Conclusions**

We have found that overlayer structures formed during the adsorption of P on Ni(111) depends on the coverage, the annealing temperature and time. When the sample is heated between 373 K and 673 K, the \( \sqrt{7} \times \sqrt{7} \) \( R \) 19.1° reconstructed structure is created. Annealing at temperatures above 673 K leads to the

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**Figure 6.** (a) The rectangular overlayer lattice points (red) with lattice vectors \((\overrightarrow{c_1}, \overrightarrow{c_2})\). The blue circles are the lattice points of the \( \sqrt{7} \times \sqrt{7} \) \( R \) 19.1° structure with lattice vectors \((\overrightarrow{b_1}, \overrightarrow{b_2})\). (b) Reciprocal space of (a). The white spots indicate multiple scattering. (c) Lattice unit vectors 6 domains.
formation of pattern B, where the spots in the $\sqrt{7} \times \sqrt{7} R 19.1^\circ$ pattern are split into three spots. The degree of separation and position of the three spots continue to change with temperature and annealing time. At higher temperatures, pattern C is produced where every two of the twelve sets of the three split spots in pattern B merge to give a pattern with six sets of five spots each. We have proposed a new interpretation of the $\sqrt{7} \times \sqrt{7} R 19.1^\circ$ structure based on a rectangular unit cell, which can explain the successive changes to pattern B and pattern C. The rectangular unit is similar to the local structure of P on the Ni$_2$P (1120) plane, and it can be regarded as the model structure for the Ni$_2$P surface.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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