

A MODEL OF STRUCTURES OF MONOLAYERS ADSORBED ON (100) FACES OF METALS

A comparative study of various systems in the high symmetry coincidence mesh hypothesis

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Recently, Huber and Oudar, have proposed a model for the structure of certain adsorbed layers. They have shown that an interpretation of LEED patterns based on the high symmetry of the coincidence mesh and a minimum number of different kinds of adsorption site gives rise to a structure of the adsorbate in rows or polygons. We propose here the application of the same model in the case of adsorption of a metal on (100) faces of cubic metals. We show that without knowing accurately the concentrations, but only the succession of the patterns, it is possible to deduce a model for the adsorbed layer. We give a classification of the different structures.

1. Introduction

The structure of the surface of a crystal, either clean or covered with foreign atoms, is not yet solved in the general case. For example the structure of the clean (111) faces of germanium and silicon are still under discussion. The hypothesis formulated by Lander [1] explaining the silicon $p(7\times 7)$ structure by an arrangement of vacancies has been favourably reexamined [2]. On the other hand, for the case of a metal on a metal up till now most authors have considered that the adsorbed atoms are uniformly distributed on the crystal surface. They consider that at low coverage the adatoms are located at sites of high coordination, and that at high coverages the structure of the adsorbed layer is approximately a closed packed hexagonal or square arrangement [3–6]. Other models such as high-symmetry layer with vacancies, have not been considered.

The problem of the reconstruction of adsorbed layers is also under discussion.

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Many authors [7–11] have supposed that the surface of a crystal is reconstructed on adsorption. With the development of the theory of low energy electron diffraction, it is now possible in simple cases to determine with a degree of confidence the structure of the adsorbed layer. Theoretical calculations have been made only for the $c(2 \times 2)$ [or $p(\sqrt{2} \times \sqrt{2})45^\circ$] and $p(2 \times 2)$ cases on the simple faces of metals. McDonnell et al. [12] find good agreement between theory and experiment with a reconstructed surface in the case of adsorption of oxygen on copper (100). The mixed layer being at a distance of the substrate 5 or 10 per cent larger than the interplanar spacing. For sulfur on nickel (100), Demuth et al. [13] propose that the sulfur atoms of the $c(2 \times 2)$ structure are located in the four-fold symmetry sites, at a distance of $1.3 \pm 0.1 \text{ \AA}$ from the substrate. If we suppose that the sulfur and nickel atoms are both spherical, then the diameter of the sulfur atom is 1.8 \AA . This is much smaller than the diameter usually taken in models of adsorbed sulfur. This is a possible explanation of the experimental measurement of the low screening of the sulfur adsorbed on metals [14].

Ignatiev et al. [15] have calculated that the $c(2 \times 2)$ selenium layer adsorbed on the (100) face of silver is in the four-fold symmetry sites at a distance of 1.91 \AA from the substrate. The adsorbed selenium atoms have then a diameter of 2.7 \AA smaller than the one expected. In the case of chlorine adsorbed on the (100) face of tungsten [16], the authors have used the theory of the diffraction of the periodic antiphases by X-rays [17]. They deduce that the chlorine atoms are located in the two-fold symmetry sites (bridge position) and not in the four-fold symmetry sites.

The above examples show that there is no evidence for a general solution of the real position of adsorbed atoms even in simple cases like the $c(2 \times 2)$ structure on (100) surfaces.

Recently, Huber and Oudar (referred to as H–O) [18] have suggested a new approach to the structure of adsorbed layers by considering both the high symmetry of the coincidence mesh and the minimum number of different kinds of adsorption sites. They have shown that in some cases the surface layer of the substrate can be slightly modified to produce new adsorption sites. To have a minimum number of possible solutions (preferably one), it is necessary to know the number of atoms per cell accurately. This is not always possible but in some cases one can have a good estimation by taking into account the succession of structures. For example, the $c(2 \times 2)$ structure on (100) faces can be reasonably assumed to represent half a monolayer, and later structures will therefore be denser.

In this paper, we have taken data from various authors and with the ideas developed by H–O [18], we intend to give a classification of the various structures obtained on the (100) surfaces of different metals, with the additional assumption of a simple adsorption on an undisturbed substrate.

2. The structures p or $c(n\sqrt{2}\times\sqrt{2})45^\circ$

In order to give a general description of these structures, we shall use the experimental results of Bibérian and Rhead [6] obtained during the deposition of lead on the (100) face of gold. They describe the following sequence of structures: $c(2\times 2) \rightarrow c(7\sqrt{2}\times\sqrt{2})45^\circ \rightarrow c(3\sqrt{2}\times\sqrt{2})45^\circ$. In the case of a metal adsorbed on a metal, at low coverage it is highly probable that due to the metallic bond between the adatoms and the substrate, the adsorbed atoms are in the four-fold symmetry sites. Fig. 1 gives the reciprocal lattice and the position of the adsorbed atoms in the case of the $p(\sqrt{2}\times\sqrt{2})45^\circ$ or $c(2\times 2)$ structure. The fraction of sites occupied is $\theta = 0.5$.

When the coverage increases, the $c(7\sqrt{2}\times\sqrt{2})45^\circ$ structure appears. Fig. 2 shows that in such a case we have 7 four-fold symmetry sites per unit mesh. As the previous structure $p(\sqrt{2}\times\sqrt{2})45^\circ$ had $\theta = 1/2$, the only possibilities here are $4/7$ or $5/7$. To clarify this point, we can have a look to the next structure which is $c(3\sqrt{2}\times\sqrt{2})45^\circ$. Fig. 3 shows that we have then only 3 sites per unit cell. The only possibility is then $\theta = 2/3$. Because of the increasing coverage we must have $1/2 < n/7 < 2/3$, therefore $n = 4$. This coverage is in agreement with an estimation

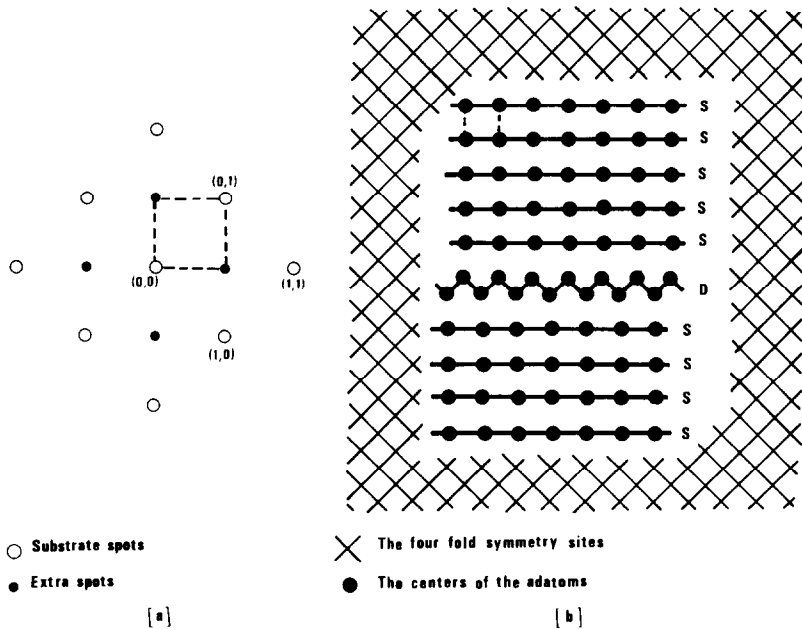


Fig. 1. $p(\sqrt{2}\times\sqrt{2})45^\circ$ or $c(2\times 2)$ or $(\frac{1}{2}\frac{1}{2})$ structure. (a) The reciprocal lattice; in dashed lines, the reciprocal unit mesh. (b) The direct lattice; two domains in antiphase, each one is composed of single rows (S) and they are separated by a double row (D).

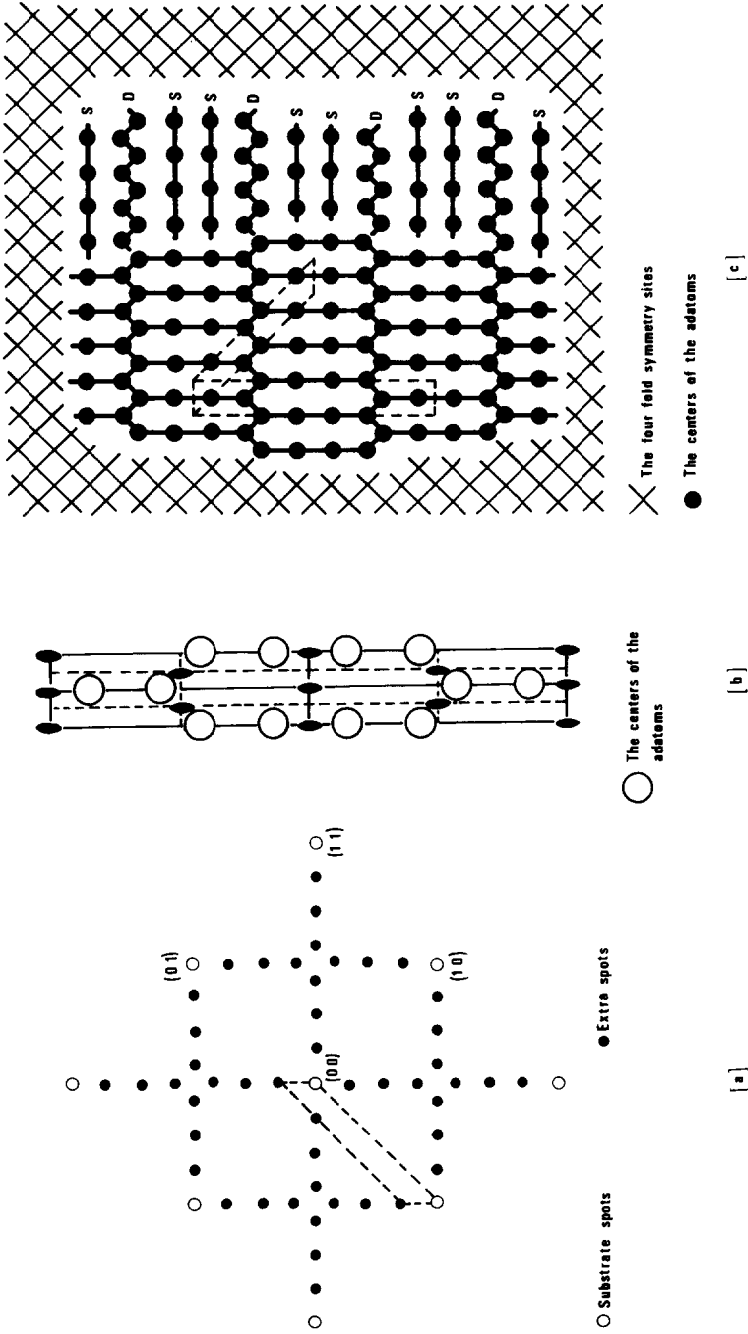


Fig. 2. $c(7\sqrt{2} \times \sqrt{2})45^\circ$ or $(4\sqrt{3})$ structure. (a) The reciprocal lattice, with the two orthogonal domains; in dashed lines, the reciprocal unit mesh. (b) The $c2mm$ two-dimensional space group with the position of the adatoms. (c) The direct lattice, composed of hexagons, or an alternation of single rows (S) and double rows (D).

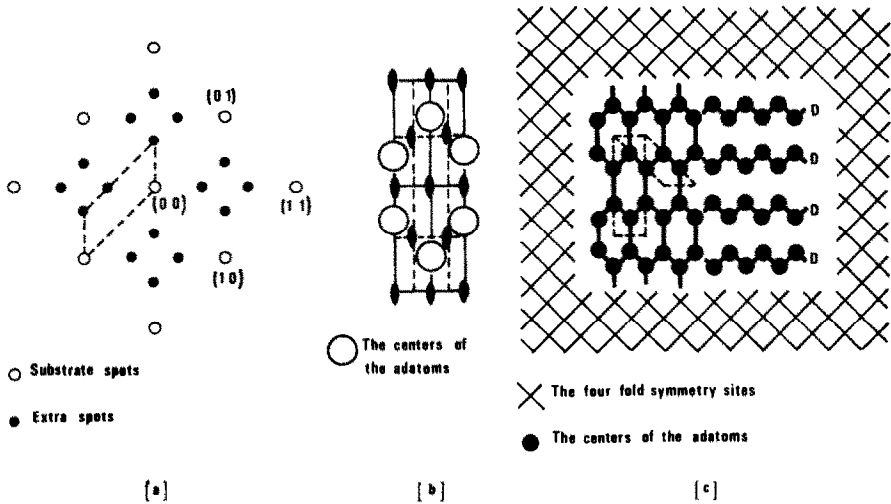


Fig. 3. $c(3\sqrt{2} \times \sqrt{2})45^\circ$ or $(\frac{2}{1} \frac{1}{1})$ structure. (a) The reciprocal lattice, with the two orthogonal domains; in dashed lines, the reciprocal unit mesh. (b) The $c2mm$ two-dimensional space group with the position of the adatoms. (c) The direct lattice, composed of hexagons, or double rows (D).

deduced from the evaporation time.

There are two rectangular centered two dimensional space groups [19]: the group $c1m1$ has a low symmetry, and the group $c2mm$ has a high symmetry. Fig. 2 gives a model for the atomic positions and shows the various elements of symmetry in the $c2mm$ group. One can interpret this model as a surface filled with non regular hexagons of lead, or by a succession of single rows (S) and double rows (D) of lead atoms. In short we can designate this structure by a formula, S_2D (S-S-D-S-S-D-S-S-...).

One can consider in the same way that the $p(\sqrt{2} \times \sqrt{2})45^\circ$ structure is formed by S rows. Fig. 1b shows that the boundary between two domains in antiphase is a D row.

Similarly we can give an analogous model for the $c(3\sqrt{2} \times \sqrt{2})45^\circ$ structure. The interpretation is the same, but in this case we have only D rows (see fig. 3).

H-O [18] have given a similar explanation for the adsorption of sulfur on (100) iron. They interpreted in this way the $c(11\sqrt{2} \times \sqrt{2})45^\circ$, $c(9\sqrt{2} \times \sqrt{2})45^\circ$, $c(7\sqrt{2} \times \sqrt{2})45^\circ$, $c(5\sqrt{2} \times \sqrt{2})45^\circ$, structures discovered by Margot et al. [9]. We can give these the formulae S_4D , S_3D , S_2D , SD respectively.

During the adsorption of lead on copper (100), Henrion and Rhead [5] observed the $c(5\sqrt{2} \times \sqrt{2})45^\circ$ structure which can be interpreted with the same model and the formula SD . This structure has been also observed by Perdereau and Szymerska [4] during the adsorption of lead on (100) nickel.

Table 1

Structure		Space group	Experiments	θ	Formula	n
Matricial notation	Wood's notation					
$\begin{pmatrix} 2 & \bar{1} \\ 1 & 1 \end{pmatrix}$	$c(3\sqrt{2} \times \sqrt{2})45^\circ$	c2mm	Au/Pb [6]	$2/3 = 0.667$	D	3
$\begin{pmatrix} 3 & \bar{2} \\ 1 & 1 \end{pmatrix}$	$c(5\sqrt{2} \times \sqrt{2})45^\circ$	c2mm	Cu/Pb [5], Fe/S [9], Ni/Pb [4]	$3/5 = 0.6$	DS	5
$\begin{pmatrix} 4 & \bar{3} \\ 1 & 1 \end{pmatrix}$	$c(7\sqrt{2} \times \sqrt{2})45^\circ$	c2mm	Au/Pb [6], Fe/S [9]	$4/7 = 0.571$	DS ₂	7 n odd
$\begin{pmatrix} 5 & \bar{4} \\ 1 & 1 \end{pmatrix}$	$c(9\sqrt{2} \times \sqrt{2})45^\circ$	c2mm	Cu/Bi [3], Fe/S [9]	$5/9 = 0.556$	DS ₃	9
$\begin{pmatrix} 6 & \bar{5} \\ 1 & 1 \end{pmatrix}$	$c(11\sqrt{2} \times \sqrt{2})45^\circ$	c2mm	Fe/S [9]	$6/11 = 0.545$	DS ₄	11
$\begin{pmatrix} 2 & \bar{2} \\ 1 & 1 \end{pmatrix}$	$p(2\sqrt{2} \times \sqrt{2})45^\circ$	p2mm	Cu/O ₂ [21], Pt/O ₂ [22]	$3/4 = 0.75$	T	4 n and $n/2$
$\begin{pmatrix} 4 & \bar{4} \\ 1 & 1 \end{pmatrix}$	$p(4\sqrt{2} \times \sqrt{2})45^\circ$	p2mm	Fe/S [9]	$5/8 = 0.625$	SD ₂	8 even
$\begin{pmatrix} 1 & \bar{1} \\ 1 & 1 \end{pmatrix}$	$p(\sqrt{2} \times \sqrt{2})45^\circ$	p2mm	Many experiments	$1/2 = 0.5$	S	2 n even
$\begin{pmatrix} 3 & \bar{3} \\ 1 & 1 \end{pmatrix}$	$c(2 \times 2)$ $p(3\sqrt{2} \times \sqrt{2})45^\circ$	p2mm	Pt/CO [24, 25]	$2/3 = 0.667$	TS	6 $n/2$ odd

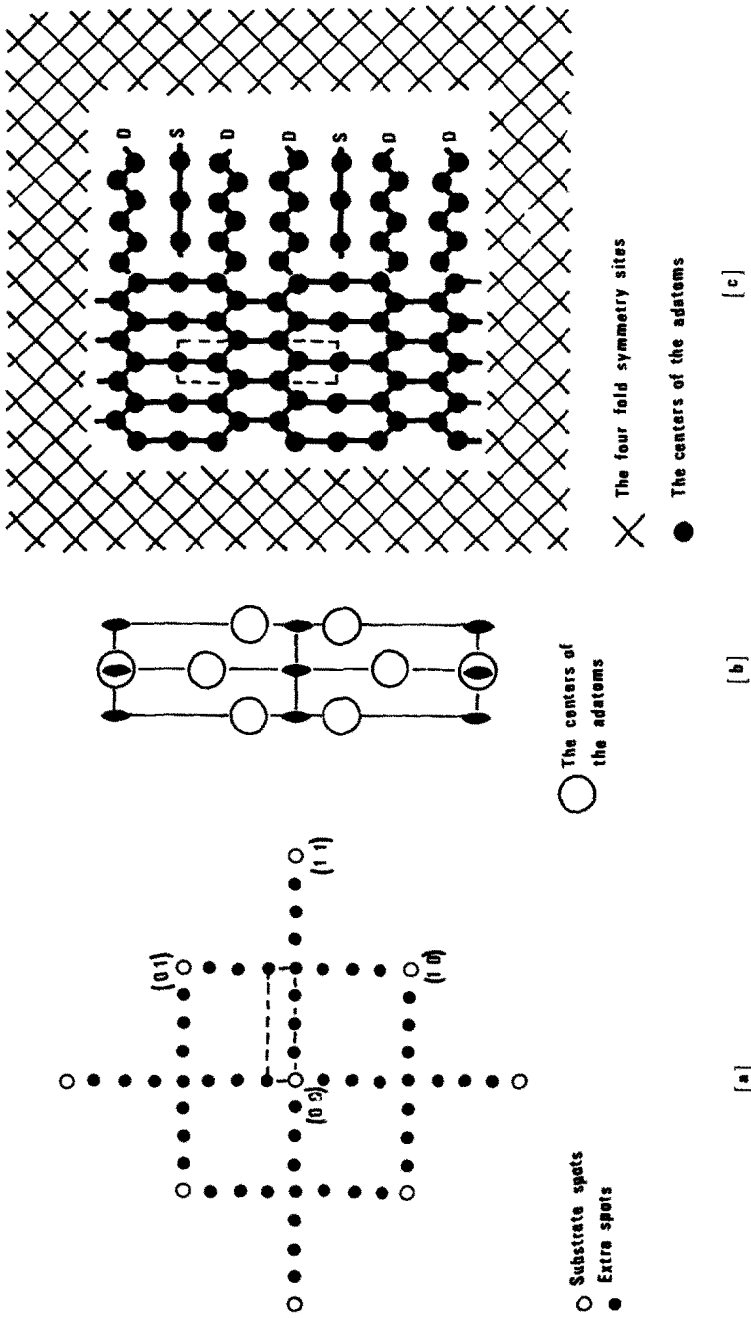


Fig. 4. $p(4\sqrt{2} \times \sqrt{2})45^\circ$ or $\begin{pmatrix} 4 & 4 \\ 1 & 1 \end{pmatrix}$ structure. (a) The reciprocal lattice with the two orthogonal domains; in dashed lines, the reciprocal unit mesh. (b) The $p2mm$ two-dimensional space group with the position of the adatoms. (c) The direct lattice composed of two kinds of hexagons, or an alternation of single rows (S) and double rows (D).

Delamare and Rhead [3] have also observed a $c(9\sqrt{2} \times \sqrt{2})45^\circ$ structure during the adsorption of bismuth on copper (100).

We have so far described here five structures $c(n\sqrt{2} \times \sqrt{2})45^\circ$ with $n = 3, 5, 7, 9, 11$. If we consider the number of extra spots along the diagonal of the reciprocal lattice plus one, this number is also n . Experimentally no structure with n larger than 11 has been seen. Table 1 gives a general view of the different structures.

Up till now we have considered the structures obtained with n odd. We shall now consider the structures with n even and $n/2$ even too. In this case according Wood's notation [20] the structure will be $p(n\sqrt{2}/2 \times \sqrt{2})45^\circ$.

For $n = 8$, H-O [18] give a model with the space group symmetry $p2mm$. Fig. 4 shows the atomic positions of the adatoms. The structure can be interpreted as an alternation of two kinds of hexagons. According to fig. 4c we can give the formula SD_2 .

In the case of adsorption of oxygen on copper (100) [21] or platinum (100) [22] we have a $p(2\sqrt{2} \times \sqrt{2})45^\circ$ structure which can be interpreted as shown in fig. 5. The fraction of sites occupied is $\theta = 0.75$. Recently Argile and Rhead [23] have studied the coadsorption of lead on copper (100) covered with oxygen. When the surface is saturated with oxygen [structure $p(2\sqrt{2} \times \sqrt{2})45^\circ$], they can still deposit a quarter of monolayer of lead. This is in agreement with the number of sites free on the surface. Fig. 5 shows the hexagonal (non regular) structure of the adsorbed layer, and it shows that we have triple rows of adatoms (T). The formula is here: T.

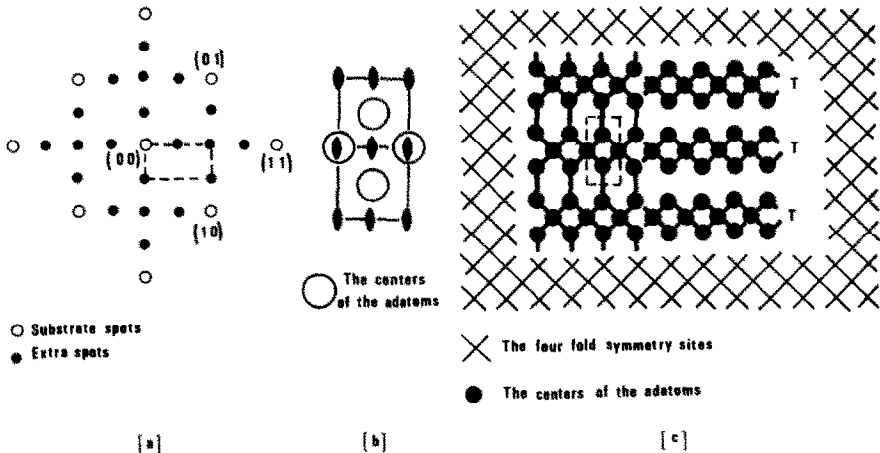


Fig. 5. $p(2\sqrt{2} \times \sqrt{2})45^\circ$ or $\begin{pmatrix} 2 & \bar{2} \\ 1 & 1 \end{pmatrix}$ structure. (a) The reciprocal lattice, with the two orthogonal domains; in dashed lines, the reciprocal unit mesh. (b) The $p2mm$ two-dimensional space group with the position of the adatoms. (c) The direct lattice composed of hexagons or triple rows (T).

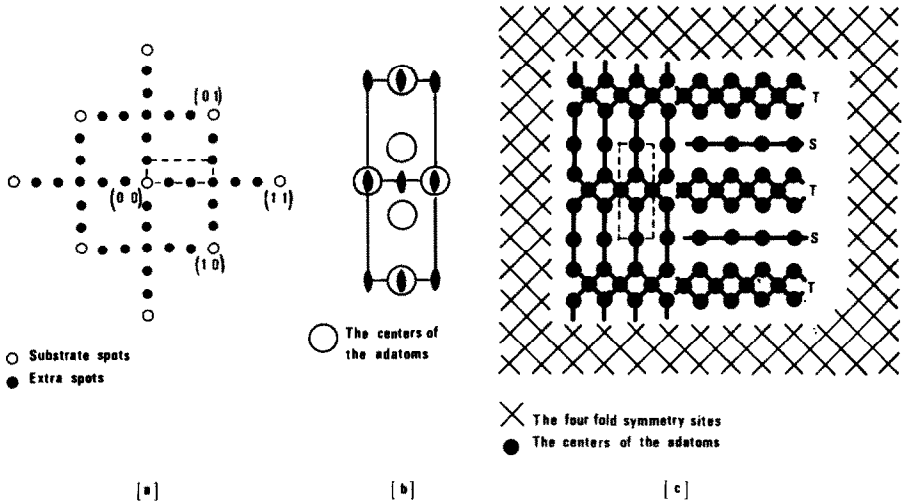


Fig. 6. $p(3\sqrt{2} \times \sqrt{2}) 45^\circ$ or $\begin{pmatrix} 3 & \bar{3} \\ 1 & 1 \end{pmatrix}$ structure. (a) The reciprocal lattice with the two orthogonal domains; in dashed lines, the reciprocal unit mesh. (b) The $p2mm$ two-dimensional space group with the position of the adatoms. (c) The direct lattice composed of hexagons or an alternation of single rows (S) and triple rows (T).

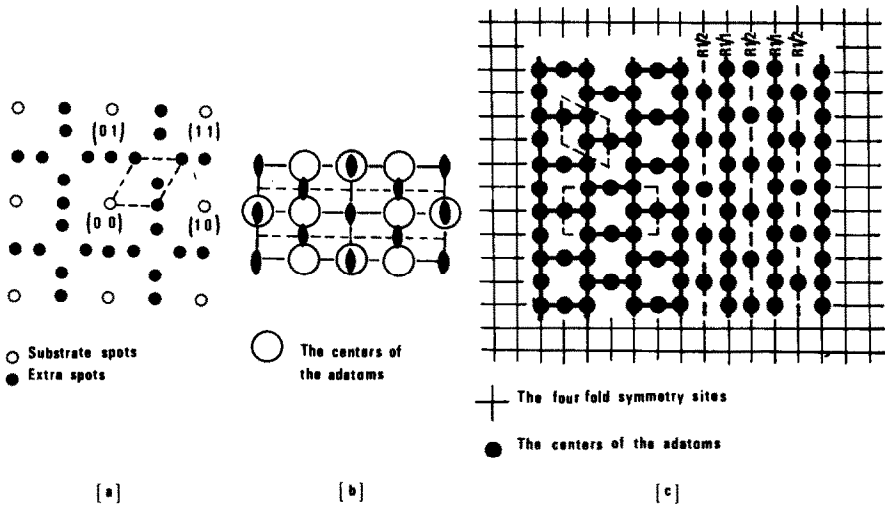


Fig. 7. $c(4 \times 2)$ or $\begin{pmatrix} 2 & \bar{1} \\ 0 & 2 \end{pmatrix}$ structure. (a) The reciprocal lattice with the two orthogonal domains; in dashed lines, the reciprocal unit mesh. (b) The $c2mm$ two-dimensional space group with the position of the adatoms. (c) The direct lattice composed of squares or an alternation of full rows (R1/1) and half full rows (R1/2).

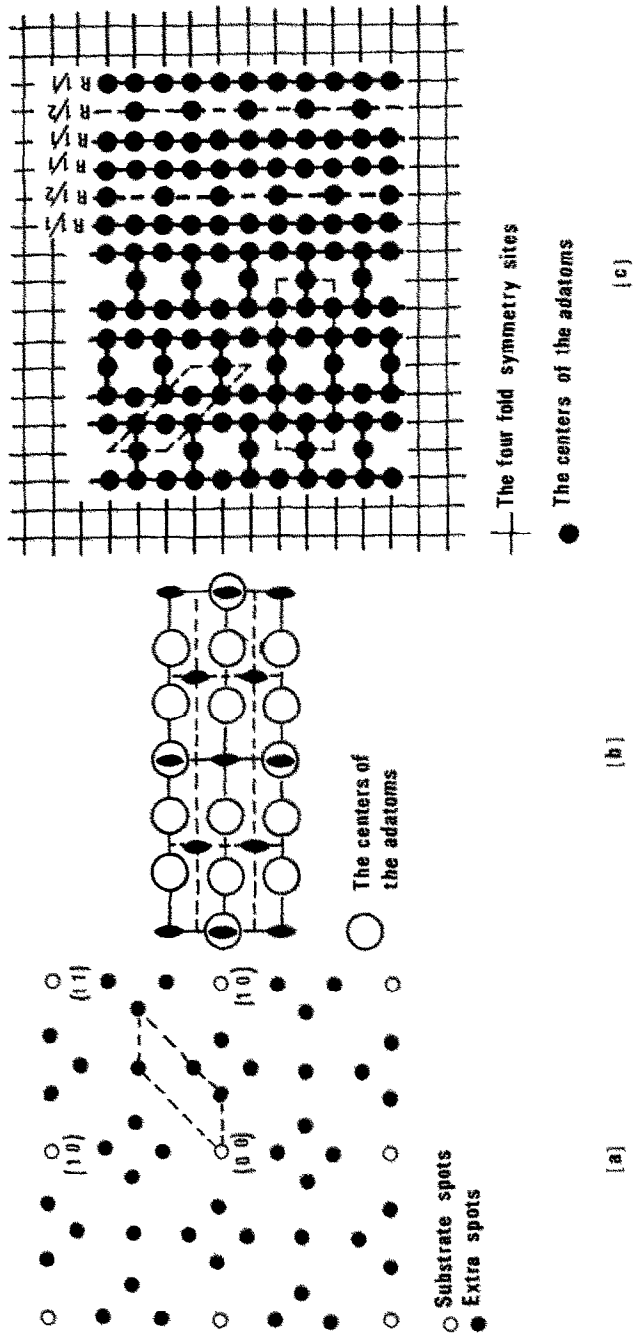


Fig. 8. $c(6 \times 2)$ or $(\frac{3}{2})$ structure. (a) The reciprocal lattice with the two orthogonal domains; in dashed lines, the reciprocal unit mesh. (b) The $c2mm$ two-dimensional space group with the position of the adatoms. (c) The direct lattice composed of squares or an alternation of full rows ($R1/1$) and half full rows ($R1/2$).

We shall now consider the case n even and $n/2$ odd. In the case of adsorption of carbon monoxide on platinum (100), we have the structure $p(3\sqrt{2} \times \sqrt{2})45^\circ$ [24, 25]. If we suppose here too that adsorption is in the four-fold symmetry sites, then this structure can be interpreted as shown in fig. 6. It shows the same structure as the previous one but with larger hexagons, and the alternation of T and S rows. The formula is then ST.

All the results have been summarized in table 1.

3. The structure p or $c(n \times m)$

As mentioned before the centered structures have only one two-dimensional space group of high symmetry: $c2mm$.

The structure $c(4 \times 2)$ has been observed for carbon monoxide adsorbed on platinum (100) [25] and bismuth on gold (100) [26]. Fig. 7 gives the details of the interpretation. It shows that we can consider the structure as formed by an arrangement of squares, and that we can interpret it also as an alternation of full rows (R1/1) and half full rows (R1/2), the formula could be (R1/1)(R1/2); here $\theta = 0.75$. Morgan and Somorjai [24] give the same model but with the CO molecules adsorbed on the bridge sites of platinum (100).

The structure $c(6 \times 2)$ exists in the case of adsorption of lead on gold (100) [6] and oxygen on molybdenum (100) [27]. Fig. 8 gives an interpretation of this struc-

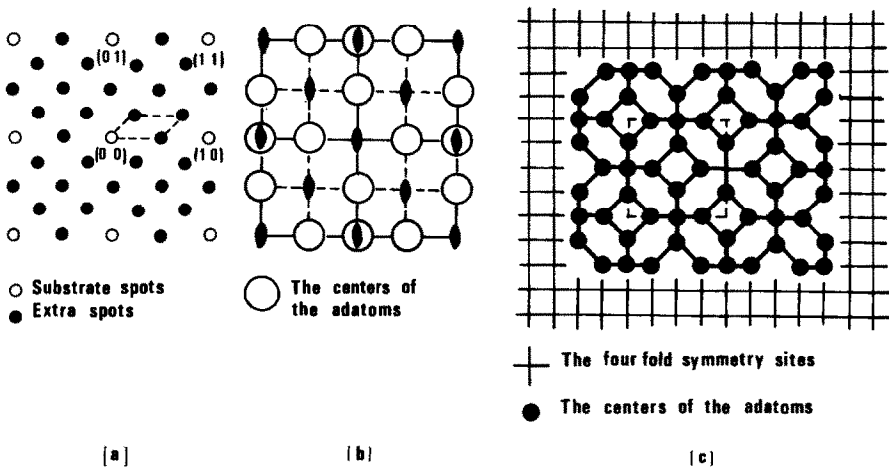


Fig. 9. $c(4 \times 4)$ or $(\frac{2}{0} \frac{2}{4})$ structure. (a) The reciprocal lattice; in dashed lines, the reciprocal unit mesh. (b) The $c2mm$ two-dimensional space group with the position of the adatoms. (c) The direct lattice composed of polygons.

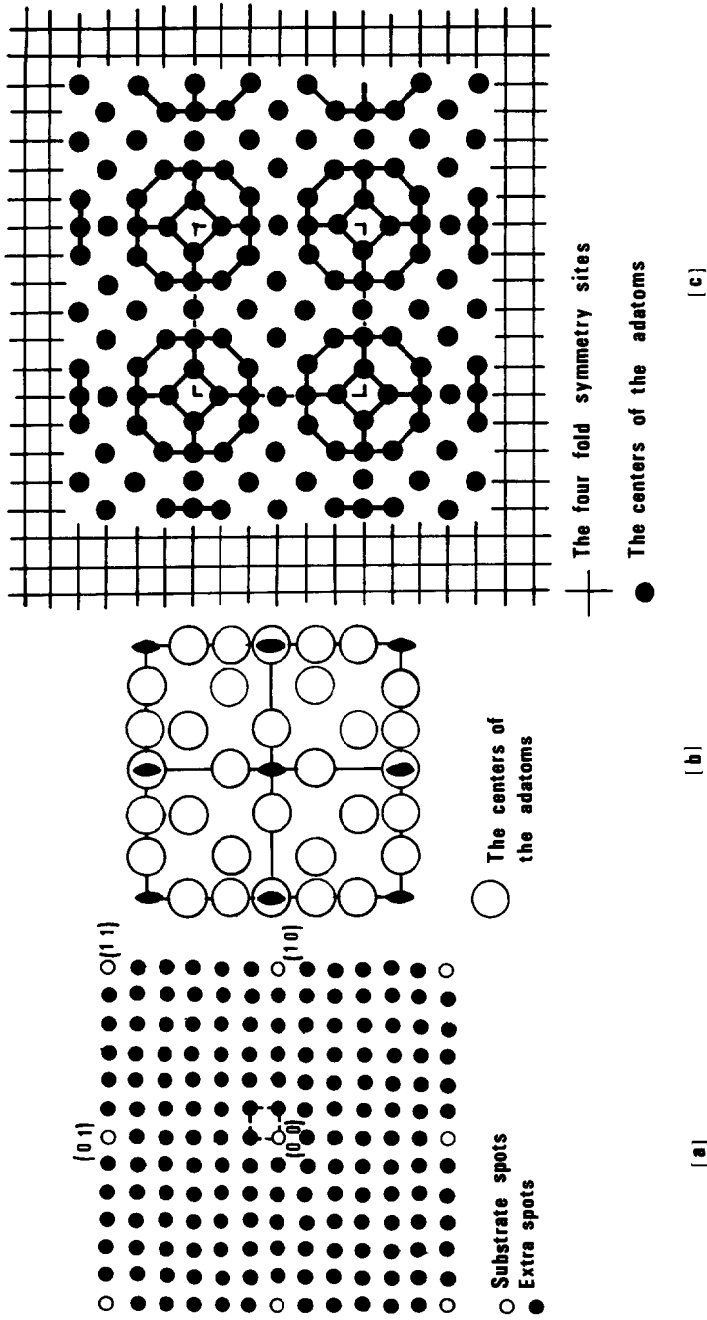


Fig. 10. $p(6 \times 6)$ or $\begin{pmatrix} 6 & 0 \\ 0 & 6 \end{pmatrix}$ structure. (a) The reciprocal lattice; in dashed lines, the reciprocal unit mesh, (b) The $p2mm$ two-dimensional space group with the position of the adatoms. (c) The direct lattice composed of polygons similar to those of the $c(4 \times 4)$ structure (see fig. 9).

ture. It shows as previously the arrangement of squares and the structure in rows with the formula $(R1/1)_2(R1/2)$. We have here $\theta = 5/6$.

During the adsorption of sulfur on gold (100) [11], the $c(4 \times 4)$ structure was observed; fig. 9 gives the details of the interpretation. Here the number of atoms shown in the unit cell has been confirmed by a radioactive method. Again the structure can be considered as an arrangement of hexagons. And here $\theta = 5/8$. In the same experiment with a lower coverage of sulfur, the authors also observed a $p(6 \times 6)$ structure simultaneously with the $c(4 \times 4)$ structure. Fig. 10 gives a model for this structure and we can see in fig. 10c the same arrangement of atoms as in the $c(4 \times 4)$ structure, and which explains the above experimental observation.

4. Conclusion

In this study we have shown that using the model described by H-O [18], it is possible to give a classification of the structures which appear during the adsorption on (100) surfaces of different metals. In fact we can distinguish two main classifications. When the coincidence mesh is rectangular, it gives rise to an alternation of infinite chains (see table 1). When the coincidence mesh is square or hexagonal, then it is better to consider the adsorbate as formed of polygons. This latter case is more difficult to classify and will be studied more deeply in other articles.

We have shown here that the series of structures described by H-O [18] in the case of sulfur on iron (100) were also a good model in other systems. We have seen how it was possible to explain the c or $p(n\sqrt{2} \times \sqrt{2})45^\circ$ structures on the basis of a $p(\sqrt{2} \times \sqrt{2})45^\circ$ structure with periodic antiphases. This is an important point, because often a particular LEED pattern has been associated with a particular phase, and here we show that in fact the apparently different structures can be due to different densities of defects of a $p(\sqrt{2} \times \sqrt{2})45^\circ$ structure.

This model of chains or polygons has been proposed already to explain the structures of clean surfaces like silicon. Lander [1] gave a model of the $p(7 \times 7)$ structure of silicon (111) with 13 vacancies, the symmetry of the surface layer being $p3m1$. This model creates polygons at the surface. Phillips [2] has calculated that energetically a silicon or germanium surface is more stable with vacancies, and he shows that there appear polygons and chains at the surface. He gives as a proof of his idea the fact that at a temperature around half of the melting temperature, the superstructure disappears and the (1×1) structure appears; he interprets this as a melting of the first layer. This has been observed by Henrion and Rhead [5], with the melting of a lead monolayer adsorbed on copper.

Some of the most important criticism that can be made of the high symmetry model is that quite often the adatoms are very close in comparison with the usual diameters. This point has already been explained by H-O [18]: they suppose that in fact the adatoms can move in the vertical position or parallel to the surface while still respecting the symmetries. There is also no evidence that adsorbed atoms are

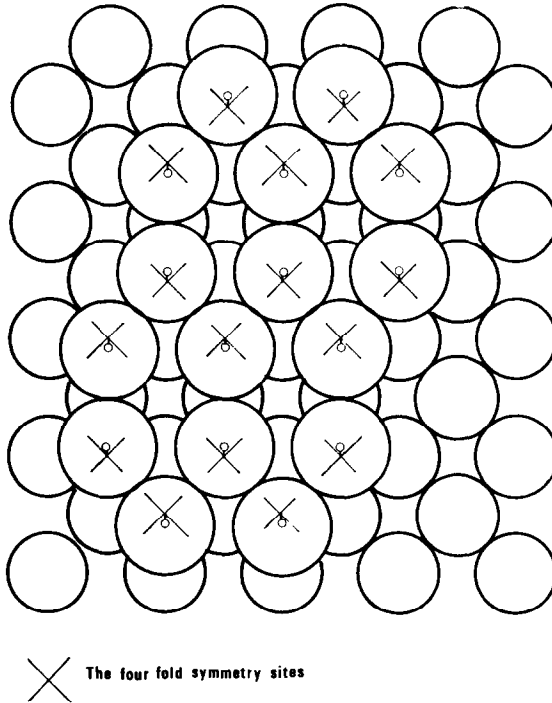


Fig. 11. $c(3\sqrt{2} \times \sqrt{2})45^\circ$ or $\begin{pmatrix} 2 & 1 \\ 1 & 1 \end{pmatrix}$ structure. Small circles: the substrate atoms; large circles: the adatoms. The arrows show the displacements of the adatoms from the four-fold symmetry sites.

spherical, they may be deformed by the substrate in agreement with the symmetries. The application of coloured groups to the adsorbate and the first layer of the substrate can give indications of the way the atoms move. For instance, in the case of adsorption of lead on gold (100), for the $c(3\sqrt{2} \times \sqrt{2})45^\circ$ structure, the distance between the four-fold symmetry sites is too small, because the ratio between the diameters of the lead atoms to the gold atoms is 1.21. Fig. 11 shows how a small displacement of the lead atoms in the [110] direction can allow the adsorption with the same symmetry. In the case of adsorption of sulfur or selenium, we have shown that according to recent calculations and with the hypothesis of spherical atoms, the diameters of the adsorbates are smaller than the ones expected.

From a theoretical point of view, the high symmetry model will allow easier calculations of the LEED intensities because of the small number of different kinds of adatoms. For instance, in the case of lead on gold (100), for the $c(3\sqrt{2} \times \sqrt{2})45^\circ$ structure, there is only one kind of adatom, and two parameters, the altitude and the displacement in the [110] direction. As confidence in LEED calculations in-

creases, structures of this type could provide important tests.

Recently, Peralta et al. [28] have studied the adsorption of sulfur on molybdenum (110), and they give an analogous model for their interpretation.

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