Submitted to Journal of Chemical Physics

UCRL-19638
Preprint

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May 1970

AEC Contract No. W-7405-eng-48

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Simple Rules to Predict the Structure of Adsorbed Gases on Crystal Surfaces.

by

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Abstract

The surface structures of adsorbed gases on crystal surfaces which were detected by low energy electron diffraction have been reviewed. From the analysis of the available structural data three rules of ordering have been proposed. The close-packing rule indicates that adsorbate-adsorbate interaction plays an important role in ordering. The rules of rotational symmetry and similar unit cell vectors are the consequence of the substrate-absorbate interaction. Judicious application of these rules should allow one to predict the surface structures of adsorbed gases and condensable vapors which would form on crystal surfaces. It appears that both the heat of adsorption and the activation energy for surface diffusion of the adsorbed molecules influences ordering on surfaces.

Introduction

Low energy electron diffraction studies have uncovered that chemisorption predominantly yields ordered structures on single crystal surfaces (which are commonly called "substrates"). The surface structure which forms, depend, to a great extent, on the symmetry of the substrate, the chemistry and size of the adsorbed gas molecule, and in some cases the surface concentration of the adsorbate (which may be controlled by the gas partial pressure over the surface). In recent years a great deal of data has been accumulated on the surface structures of adsorbed gases mostly on those which form on the lowest index (highest density) faces of face-centered cubic and body-centered cubic crystal surfaces, although some experimental studies have been carried out on low-index diamond and close packed hexagonal crystal surfaces.[1] Since virtually countless numbers of surface structures may form upon adsorption of various gases on different crystal faces of monatomic and polyatomic solids with various crystal structures, they cannot all be studied by experiments. Indeed, many solids which might yield interesting surface structures are outside the range of convenient experimentation by low energy electron diffraction due to their high vapor pressure (for example, cesium or iodine). Some of the substrates of interest may not be easily available in single crystal form. The experimental data which have been accumulated so far indicate several regularities or trends which are operative in the formation of surface structures of adsorbed gases on high density crystal planes. The purpose of this paper is to summarize the available experimental data on the surface structures which form during chemisorption of non-condensable gases and to propose a set

of rules which appear to govern the formation of ordered surface structures. It is hoped that the application of these rules to other substrate-adsorbate systems which have not been studied so far will allow one to predict the surface structures which should form.

Most of the adsorbed gases which we shall consider have molecular dimensions which are smaller than or similar in size to the largest inter-row distances in the substrate crystal surfaces. Thus, these molecules or atoms may easily "fit" unto the surface without the need of overlapping several substrate atoms. The gases are oxygen, carbon monoxide, hydrogen, nitrogen, ammonia, and carbon dioxide, which may adsorb as molecules or in a dissociated form. Recently,[2] longer-chain olefins with large molecular dimensions have been studied, and they will also be included in the analysis.

It should be noted that there are systems which represent exceptions to the rules of ordering which are being proposed. These exceptions will be pointed out and discussed wherever possible. In addition, cases have been observed in which the adsorption of a gas does not yield an ordered surface structure (for example, oxygen adsorption on aluminum surfaces). Those rare cases in which chemisorption yields amorphous surface structures are excluded from our consideration.

A Simple Nomenclature of Surface Structures.

The total symmetry of a crystal surface is described by the combination of the Bravais lattices and the crystallographic point groups. There are 17 unique and allowed combinations of the five Bravais lattice and ten crystallographic point groups. There are called two dimensional space groups. The reader is referred to an excellent discussion of these space groups by Wood.[5]

A Simple Nomenclature of Surface Structures.

In most cases, studies were carried out only on low index (highest density) crystal orientations of monatomic solids of high crystal symmetry. In Figs. 1, 2, and 3 surfaces are shown which exhibit six-fold, four-fold, and two-fold rotational symmetries. In considering the structures of adsorbed molecules on surfaces of high symmetry, we can use the simple notation which is applied widely in the literature.[1,3,4] If the surface structure, which forms in the presence of an adsorbed gas, is characterized by a unit cell which is identical to the primitive unit cell of the substrate, the surface structure is denoted (1x1) (Fig. 1a). A (2x2) surface structure is formed if the unit cell dimensions of the structure is twice as large as the substrate unit cell. The appearance of a diffraction pattern which is characteristic of this structure often indicates that the adsorbed atoms occupy every second lattice site on the substrate (Figs. 1b and 2a). If every third lattice site on a hexagonal face is distinguished from the other sites by selective adsorption then a $(\sqrt{3} \times \sqrt{3})$ R - 30° surface structure may arise (Fig. 1c). The angle after the (nxn) notation indicates the orientation of the new unit cell relative to the substrate unit cell. If every other lattice site on a square face is unique and occupied by a chemisorbed atom, then a $(\sqrt{2} \times \sqrt{2})$ R - 45° surface structure could be formed. To avoid a non-integer notation for this frequently occurring surface structure it is usually labelled as c (2x2) where the c indicates that it is a centered (2x2) structure (Fig. 2b). Often surface structures will exist that have the dimensions of the substrate unit cell along one

translation on the surface but a larger dimension along the other translation direction. These structures are frequently denoted as being (1xn), where the one indicates the usual bulk unit cell dimensions or substrate cell dimension along the x direction, while the n indicates n times the substrate unit cell dimension along the y direction (Fig. 3c where n = 3). When both unit cell vectors of the substrate are of the same magnitude (as on the (100) face of the f.c.c. or b.c.c. solids for example), then it is possible to have two types of domains; one set of the (1xn) and one set of the (nx1) kind. In most cases the diffraction pattern arising from a surface which exhibits both, (nx1) and (1xn) domains is distinguishable from a diffraction pattern arising from a (nxn) surface structure. For example, a (1x2) surface structure on a substrate with a square unit cell may contain two types of domains rotated relative to one another by 90° and giving rise to $(0\frac{1}{2})$ and $(\frac{1}{2}0)$ spots. A true (2x2) structure however will give rise to $(\frac{1}{2}\frac{1}{2})$ spots in addition to those which appear for the domain structures. Surface structures of the type (nxm) where $n \neq m$ are frequently formed. For example, carbon monoxide on a Pd (100) face gives a c(4x2) structure. On substrates which are characterized by unit cell vectors of unequal magnitude (for example f.c.c. (110) or b.c.c. (211) surfaces), surface structures of the (nxm) type where $n \neq m$ are formed most frequently. If the surface structure is known to be associated with the adsorbed gas or condensate (this is the situation we are considering) it is customary to denote the adsorbate material in the description of the surface structure as (nxm) - S where S is the chemical symbol or formula for the adsorbate. Perhaps one of the simplest examples of this would be the oxygen surface structure on molybdenum where the oxygen atoms or molecules on the surface of the metal have the same unit mesh as the clean metal surface. This structure would

be denoted as the Mo(100)-(1x1)-O structure the chemical symbol and crystallographic face of the substrate being given first, then the unit mesh of the surface structure relative to that of the substrate, and finally the chemical symbol of the adsorbate is denoted.

A useful and simple method for determining the real space lattice of the surface structure from its reciprocal lattice vectors as displayed in diffraction pattern has been developed.[6] This method is based on the inverse relationship between the reciprocal lattice matrix and the real space matrix and is excellent for the analysis of complicated surface structures. Since most of the structures which are being considered in this paper are simple and can be identified by the short-hand notations which we have described above, the surface structures will not be discussed in terms of the matrix notation.

Surface Structures of Adsorbed Gases.

In Tables I, II, and III, the surface structures which form upon the chemisorption of gases on different crystal surfaces are listed for those solids which have been investigated by low energy electron diffraction. All of the surface structures listed were judged reproducible by the investigators. First we list those surface structures which have formed on substrates exhibiting six-fold rotational symmetry (Table I). This is followed by a tabulation of the surface structures which have formed on substrates exhibiting four-fold and two-fold rotational symmetry (Table II & III).

There are several rules which appear to be applicable to the formation of most of these ordered structures of chemisorbed gases. If they are applied judiciously they can predict the type of surface structure which is to form in many chemisorbed systems. These rules are empirical and

were formulated from the correlation of existing surface structural data. Nevertheless the physical-chemical reasoning which permits one to propose these "rules of ordering" is clear. It appears that chemisorption leads to the formation of surface structures which exhibit maximal adsorbate-adsorbate and adsorbate-substrate interactions.

Rule of Close-packing.

Adsorbed atoms or molecules tend to form surface structures characterized by the smallest unit cells which are permitted by molecular dimensions, adsorbate-adsorbate and adsorbate-substrate interactions. They prefer close-packing arrangements.

Inspection of the tables reveal the absence of surface structures with large unit cells. The structures which are most dominant are those where the unit cell size is the same (1x1) or approximately twice as large as the substrate unit cell $\left[(2x2),\ c(2x2),\ (\sqrt{3} \times \sqrt{3}),\ (2x1)\right]$. The adsorbed atoms seem to pack as closely as allowed by the interactions between adsorbate molecules and the interactions with the substrate. The preferred close packing arrangement indicates that the adsorbate-adsorbate interactions for the molecules which were investigated by low energy electron diffraction is just as strong as the adsorbate-substrate interaction and plays an important role in the surface binding process.

There are several co-adsorbed gas surface structures where both adsorbed species participate in the surface structure. These surface structures are formed during the simultaneous adsorption of two gases and would not form in the presence of only one or the other gas component. The appearance of such mixed surface structures indicates that there is a strong interaction within the adsorbed layers between the different molecules.

These structures form most frequently when both gases which are being adsorbed have approximately equal probability of adsorption. If one gas adsorbs more strongly than the other (for example, during the co-adsorption of xenon and carbon monoxide) then one finds that the more tenacious species, (carbon monoxide) will replace and displace the other species, (xenon) adsorbed on the surface if they are introduced in nearly equal amounts.* The simultaneous adsorption of nitrogen and carbon monoxide on the (100) surface of tungsten yields a surface structures which cannot be formed by the individual gases.[52] Similar results were obtained by the co-adsorption of oxygen and carbon monoxide on the W (110) face[87] or hydrogen and carbon monoxide on the Pt (100) face.[43,45] The phenomenon of co-adsorption also shows the importance of close packing of the adsorbates in forming their ordered surface structures.

Adsorbed molecules whose dimensions are larger than the largest inter-row spacing in the substrate surface also form the smallest possible unit cells. For example, propylene, 2-butenes (cis and trans), isobutylene and butadiene form (2x1) and (2x2) surface structures on the (111) face

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* Since carbon monoxide and hydrogen are both major components of the ambient, it is likely that some of the surface structures which have been reported are due to one adsorbate is actually a co-adsorbed structure.

of platinum.[2] These are the smallest unit cells which can be formed which are compatible with the size of the molecules. This indicates that the large olefin molecules pack as close as possible on the surface. On the (100) surface of platinum these olefins adsorbed in a disordered manner even though the surface concentrations are similar to that on the (111) face as indicated by work function measurements.[2] It appears that if ordering under close packing conditions is difficult due to steric hindrances to rotation in the surface layer, the adsorbed layer will be disordered rather than forming a more open ordered surface structure with a large size unit cell. This observation again indicates that the adsorbed molecules listed in the tables prefer close packing arrangements on the surface of different substrates.

There are certain difficulties which arise when one attempts to apply this rule for all of the chemisorbed structures. There are molecules which exhibit more than one binding state on a given surface. Carbon monoxide for example has at least two binding states on the (100) surfaces of different metals[2] as indicated by the variety of surface structures formed on that face as a function of temperature and partial pressure of carbon monoxide. On the other hand, on the (111) face, one binding state seems to be preferred.[2,8,29] Both, dissociated ammonia on the tungsten surface[76] and carbon monoxide on the palladium (100) surface[46] form structures which are stretched or compressed without changing the configuration of the adsorbed atoms as a functions of temperature.

The dissociation of the adsorbate may lead to chemical changes in the adsorbate molecules and in the substrate structure which modify the surface structure. For example the dissociation of olefins[2,43] or the disproportionation of CO to C and CO_2[78] leads to carbon deposition which greatly effects the

structure of the substrate and the adsorbate. Formation of nitrides[25] or carbides[21] at the surface would influence the nature of the adsorbate structure. These difficulties should be considered and taken into account when applying the close packing rule to predict the nature of ordered surface structures.

In some experiments the diffraction pattern indicates the presence of large unit cells. For example, during the carburization of tungsten, both the (110) and (100) crystal face exhibited a (5x1) surface structure.[21] Outside the field of chemisorption, similar (5x1) surface structures were detected on the clean gold, platinum and iridium (100) surfaces.[1] A (7x7) surface structuce is detected on the clean (111) face of silicon on surface structures with large unit cells are detectable in germanium surfaces as well.[1,4] Aluminum oxide, Al_2O_3, also exhibits large surface unit cells.[88,89] Its (0001) face shows a ($\sqrt{31} \times \sqrt{31}$) R ± 9° surface structure upon heating to 1200°C in vacuum. The appearance of diffraction patterns which indicate large surface unit cells are indicative of large mismatch between the surface layer and the underlying substrate which produces coincidence lattices.[89] Surface phase transformation or changes of valency of ions in the surface layer[89] while the structural and chemical properties of the bulk crystal remain unchanged can give rise to the large apparent unit cell frequently rotated by small angles with respect to the substrate unit cell. For the (5x1) surface structures, a surface phase transformation to form a hexagonal surface phase has been proposed.[1] For tungsten it is expected that carbon induces such a transformation ($b.c.c._{surf} \rightarrow h.c.p._{surf}$) since it provides excess unpaired valence electrons per atom to the metal lattice.[1] The increase in the electron concentration is thought to be the cause of most phase changes in bulk crystals. When tungsten becomes saturated with carbon

the precipitated bulk phase, W_2C, exhibits h.c.p. structure. It appears that the surface phase transformation through hexagonal distortion of the tungsten surface may occur before the bulk transformation would take place. Similar phase transformations from face-centered cubic to hexagonal close packed surface structures appear to be responsible for the appearance of the (5x1) surface structure in the clean (100) faces of gold, platinum and iridium.[1] The (7x7) and other large apparent surface unit cells are thought to be due to periodic, out-of-plane buckling of the semiconductor surfaces which again produces coincidence lattices.[80,81] The $(\sqrt{31} \times \sqrt{31})$ R $\pm$ 9° surface structure is thought to be due to a change in the chemical composition and valency in the alumina surface.[89] The α-alumina surface becomes oxygen deficient at higher temperatures and the valency of the aluminum cation is reduced to Al^{+1} or Al^{+2} from Al^{+3} with a corresponding enlargement of the cation size. Such a mismatch between the surface layer and the substrate again yields coincidence lattices and large apparent unit cells.

Rule of Rotational Symmetry.

Adsorbed atoms or molecules form ordered structures which have the same rotational symmetry as the substrate phase. The substrates on which most of the adsorption studies have been carried out show three different rotational symmetries. Some of the substrates exhibit six-fold rotational symmetry [f.c.c.(111), b.c.c(111), diamond(111), hexagonal(0001)] others have four-fold rotational axis [f.c.c.(100), b.c.c.(100)] while many have two-fold rotational symmetries [f.c.c.(110), b.c.c.(110), and (211)]. In Fig. 1 we give the surface structures which are most frequently encountered for substrates which

exhibit six-fold rotational symmetry. These are the (2x2), ($\sqrt{3} \times \sqrt{3}$) R - 30°) and the (1x1) surface structures. In every case, the surface structures follow the rotational symmetry of the substrate. In some instances domain structures may form [(2x1) for example] which correspond to closer packing of adsorbates than the (2x2) structures. In this case, all three (2x1) surface structures will be present rotated 60° to each other since their formation is equally probable. In Fig. 2 we give the two surface structures [c(2x2) and (2x2)] which are observed most frequently on the substrates with four-fold rotational symmetry. It appears from inspection of Table II that the c(2x2) surface structure is somewhat more prominent as it leads to surfaces with higher coverage (close packing). Table III shows the surface structures which were detected on crystal substrates showing two-fold rotational symmetry. In addition to the c(2x2) structure, these are all (nxm), where $n \neq m$, surface structures. Their appearance reflects the fact that the magnitude of the unit cell vectors in the x and y direction along the surface are either different [(for example, f.c.c.(110) and b.c.c.(211) crystal faces] or if they are the same, they subtend an angle of about 70° [b.c.c.(110)]. It should be noted that the surface structures which are given in Fig. 1-3 are single examples of the many structures which could yield the same diffraction patterns observed in low energy electron diffraction studies. The other similar surface structures may be displaced along the surface to superpose the substrate differently or could be displaced perpendicular to the surface to give rise to various interplanar spacings between the adsorbate and substrate.

The rule of rotational symmetry seems to apply equally well to the surface structures which form during the deposition of condensable vapors on single crystal surfaces. A large number of studies of epitaxy (ordered growth of condensable vapor deposits on single crystal substrates) have revealed that the rotational symmetry of the substrate is usually preserved even when there is lattice mismatch between the film and the substrate. For example tellurium deposited on the (111) face of copper prefers the (0001) orientation which also has six-fold rotational symmetry.[92] Aluminum grows with the (111) orientation on the Si(111) surface.[93] Deposited thorium has the same crystal orientation as the Ta(100) crystal face which was used as the substrate in the epitaxial studies.[94] There are many other examples of the maintenance of rotational symmetry during the deposition of condensable vapors which are summarized elsewhere[1].

Rule of Similar Unit Cell Vectors.

Adsorbed atoms or molecules in monolayer thickness tend to form ordered surface structures which are characterized by unit cell vectors closely related to the substrate unit cell vectors. Thus, the surface structure bears a greater similarity to the substrate structure than to the structure of the bulk condensate. Only after the deposition of several atomic layers the deposited structure will adopt the surface structure of the pure condensed solid. Closer inspection of Tables I, II, and III indicates that virtually all of the surface structures of chemisorbed gases which are listed could be identified in terms of the unit cell vectors of the substrate (with the possible exceptions of those few adsorbate structures which expand or contract as a function of temperature). All of the surface unit cells of adsorbed gases can be given

as some integral multiple of the substrate unit cell [(i.e. (2x2) surface structure], or the rotated substrate unit cell [(i.e. c(2x2) or ($\sqrt{3} \times \sqrt{3}$) R-30°]. Thus it appears that the adsorbed molecules tend to prefer arrangements in which they are accommodated in the already existing surface structure by adopting the same periodicity which characterizes the substrate structure. This rule should have notable consequences if applicable to studies of epitaxy. Gradual distortion and mismatch should be observable in atomic layers of condensates which are deposited on top of the first condensate layers (which will have a substrate-like structure), until lattice dimensions which are characteristic of the bulk condensate structure are obtained. Such a highly distorted transition layer state has been well-recognized during the epitaxial growth of several solids and has been analyzed theoretically using a dislocation model [95].

The experimental recognition that the condensed vapors have structure (lattice parameter, etc.) which is closely related to the substrate surface structure allows the preparation of thin films with unusual structure and electronic properties. It is hoped that this phenomena will be explored and utilized in studies of superconductivity, band structure and surface catalysis among others.

There is a notable exception to the similar unit cell rule which should be mentioned here. If the adsorbed layer shows partial ionization, mutual repulsion may lead to adsorption in a disordered open structure. Such a system appears to be adsorbed sodium on tungsten surfaces.[96] The adsorption of other alkali metals on metal surfaces are also likely to produce disordered deposits due to surface ionization.

The Energetics of Surface Structure Formation

When xenon, argon and krypton were adsorbed on the (110) face of silver in the temperature range - 10°to - 70°C, low energy electron diffraction studies revealed that the adsorbed layers are disordered.[97] For these gases the isosteric heats of adsorption, ΔH, at zero coverage are less than 10 kcal/mole, indicating a rather weak interaction between the adsorbed gas molecules and the metal surface (substrate). The isosteric heats of adsorption increase with increasing coverage and this increase can be attributed to attractive interaction within the adsorbate layer. During the chemisorption of most gases on different solids, the heats of adsorption are appreciably larger than those observed for the rare gases. Chemisorption is accompanied in most cases by the formation of ordered surface structures, which are easily identified and studied by low energy electron diffraction. Thus, it appears that large heats of adsorption which reflects the stronger adsorbate-substrate and adsorbate-adsorbate interactions facilitates ordering on the surface.

In addition to the heat of adsorption, the activation energy for surface diffusion, ΔE_D, of the adsorbate atoms should also be an important parameter governing ordering in the adsorbed layer. For $\Delta E_D \sim kT$ the adsorbed atoms can readily diffuse along the surface and long-range order can easily be destroyed. Surface structure formation requires the condition $\Delta E_D >> kT$, a common characteristic of chemisorbed species. It is likely that even weakly adsorbed argon or xenon atoms would form ordered surface structures at sufficiently low temperatures where their surface diffusion is inhibited.

Acknowledgements: The authors wish to thank Margaret Teng for her assistance in compiling the tables. Appreciation is also extended to the United States Atomic Energy Commission under whose auspices this work was carried out.

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Table I. SURFACE STRUCTURES ON SUBSTRATES WITH SIX-FOLD ROTATIONAL SYMMETRY

Adsorbed Gas	fcc Ni(111)	fcc Pt(111)	fcc Cu(111)	fcc UO_2(111)	bcc W(111)	diamond Si(111)-(1x1)	diamond Ge(111)	hcp Ti(0001)	hcp Re(0001)	hcp Be(0001)	hcp CdS(0001)
O_2	(7,8,9) (2x2)-O	(14,15,16,17) (2x2)-O	(18) (11x5)R5°-O	(19) (3x3)-O	(20) to (211)facets	(22,23) (1x1)	(22,27) (1x1)	(27) (1x1)	(29) (2x2)-O(CO)	(30) disord.	disordered
	(7,10) (√3x√3)R30°-O			(19) (2√3x2√3)R30°-O			(28) disordered		(29) (1x1)-O(CO)		
CO	(8) (2x2)-CO	(2) C(4x2)-CO						(27) (1x1)	(29) (2x2)-CO	(30) disord.	
H_2	(8) (1x1)-H					(24) not adsorbed				(30) not adsorb.	
	(11) disordered										
N_2	(12) not adsorbed									(30) not adsorb.	
CO_2	(10) (2x2)-CO_2										
	(10) (2x√3)-CO_2										
NH_3						(25) (8x8)-N					
C_2H_2		(2) (2x1)-C_2H_2									
C_2H_4	(13) (2x2)-C_2H_4	(2) (2x1)-C_2H_4									
C_3H_6	(13) (2x1)-C_3H_6	(2) (2x1)-C_3H_6									
	(13) (√7x√7)R19°-C										
C_2H_6	(13) (2x2)-C_2H_6										
(cis and trans) C_4H_8(2-butene)		(2) (2x2)-C_4H_8									
C_4H_6(butadiene)		(2) (2x2)-C_4H_6									
C_4H_8(isobutylene)		(2) (√7x√3)R13.9°									
CH_4					(21) (6x6)-C						
H_2S						(24) (2x2)-S					
H_2Se						(24) (2x2)-Se					
I_2						(24) (1x1)					
PH_3						(26) (6√3x6√3)-P	(25) (1x1)				
						(26) (1x1)-P					
						(26) (2√3x2√3)-P					
H_2+O_2		(7) (√3x√3)R30°									

Table II

SURFACE STRUCTURES ON SUBSTRATES WITH FOUR-FOLD ROTATIONAL SYMMETRY

Absorbed Gas	fcc Ni(100)	fcc Pt(100)-(5x1)	fcc Pd(100)	fcc Cu(100)	fcc Al(100)	fcc Rh(100)	fcc W(100)	bcc V(100)	bcc Cr(100)	bcc Mo(100)	diamond C(diamond)(100)	diamond Si(100)	diamond Ge(100)
O_2	(7,32,33,34) (2x2)-O (7,35,36,37,38) C(2x2)-O	(15) (1x1)-O (39,40,41)		(47) C(2x2)-O (47) (1x1)-O (47) (2x1)-O	(48,49,50) disordered	(51) (2x8)-O	(52) (4x1)-O (52) (2x1)-O	(57) (1x1)-O (57) (2x2)-O	(58) (2x2)-O	(54) disordered (54,60,61) C(2x2)-O (54) (1x1)-O (54,61) $\sqrt{5}$(1x1)R±26°34'-O (54) (2x2)-O (61) (1x1)-CO	(61) disordered (61) ordered	(22,23,27,63) (1x1) (22,23,27,63) (111) facets	(1x1) (22,27) (22,27) disordered
CO	(38,39,42) C(2x2)-CO	(2,47,43,44) C(4x2) (2,47,43,44) ($3\sqrt{2}$x$\sqrt{2}$)R45° (43,45) ($\sqrt{2}$x$\sqrt{5}$)R45° (43,45) (2x2)-H	(46) disordered (46) C(4x2)-CO (46) compressed			(51) (4x1)-CO	(53,52) C(2x2)-CO		(55) (2x2)-CO				
H_2	(11) disordered						(54,55) C(2x2)-H (55) (2x5)-H (55) (4x1)-H	(59) disordered		(62) C(4x2)-H (62) (1x1)-H			
N_2	(11) not adsorbed			(32) (1x1)-N			C(2x2)-N		(58) (2x2)-N	(61) (1x1)-N			
C_2H_2		(2,43) C(2x2)-C_2H_2											
C_2H_4		(2,43) C(2x2)-C_2H_4											
C_3H_6		(2) disordered											
(cis and trans) C_4H_8(2-butene)		(2) disordered											
C_4H_8 (isobutylene)		(2) disordered											
C_4H_6 (butadiene)		(2) disordered											
CO + H_2		(43,45) C(2x2)-(CO+H_2)											
CH_4							(5x1)-C						
NH_3							disordered						
							C(2x2)-NH_2						
							(1x1)-NH_2						
(CO+N_2)							(4x1)-(CO+N_2)						
I_2													

Table III

SURFACE STRUCTURES ON SUBSTRATES WITH TWO-FOLD ROTATIONAL SYMMETRY

Adsorbed Gas	fcc Ni(110)	fcc Pt(110)	fcc Cu(110)	fcc Rh(110)	bcc W(211)	bcc Ta(110)	bcc Nb(110)	bcc V(110)	bcc αFe(110)	bcc Mo(110)	bcc W(110)	bcc Ta(112)	diamond Ge(110)
O_2	(7,8,41,[illegible],67) (2x1)-O (7,11,[illegible],69) (3x1)-O (5x2)-O (7) (5x1)-O (7)	(12) (1x2) (14) (2x4)	(13,47) (2x1)-O (13) C(6x2)-O	(71,72) C(2x4)-O (71,72) C(2x6)-O (71,72) C(2x8)-O (71,72) (2x2)-O (71,72) (2x3)-O	(20) (2x1)-O (20) (4x3) (20) (1x2) (73,74) (1xn)-O n=1,2,3,4	(77) (3x1)-O (78) (3x2)R18°16'-O (78) oxides	(79) (3x1)-O (79) (3x2)R18°16'-O		(81,82) C(2x2)-O (81,82) C(3x1)-O (81) C(1x5)-O (81) (2x8)-O (82) FeO(111)(cubic) (82) γ-Fe_2O_3(spinel)	(60,61,83) (2x2)-O (60,61,83) (2x1)-O (60,61) (1x1)-O (61) C(2x2)-O	(41,[illegible],87) (2x1)-O (41,[illegible],35) C(14x7)-O (25) C(21x7)-O (25) C(48x16)-O (85) C(2x2)-O (85) (2x2)-O (85) (1x1)-O (86) disordered (86) C(9x5)-CO	(3x1)-O (73) oxides (73)	(1x1) (22,27) (22,27) disordered
CO	(7,69) (1x1)-CO				(75) C(6x4)-CO (75) (2x1)-CO (75) C(4x2)-CO	(78) disordered (78) decomposition to $C+CO_2$		(74) disordered		(61,83) (1x1)-CO (69) C(2x2)-CO		disordered (79) decomposition to (78) C+CO (1+1)-H (78)	
H_2	(11,58,69,70) 1x2)-H					(78) (1x1)-H	(80) (1x1)-H			(83) adsorbed (no structure given)			
H_2O	(70) (2x1)-H_2O												
C	(70) C(2x2)-C												
NH_3 thermal break up					(76) C(4x2)-NH_2 12% stretch								
CO_2										(69) disordered			
CH_4											(21) (15x3)-C (21) (15x12)-C		
O_2+CO - coadsorption											(87) C(11x5)-CO+O_2		
N_2						(79) not adsorbed						nitride form (78) epitaxially on (113) planes	

Figure Captions

Fig. 1a-c. Schematic diagrams of the most common surface structures appearing on substrates with six-fold rotational symmetry.

Fig. 2a-b. Schematic diagrams of the most common surface structures appearing on substrates with four-fold rotational symmetry.

Fig. 3a-c. Schematic diagrams of the most common surface structures appearing on substrates with two-fold rotational symmetry.

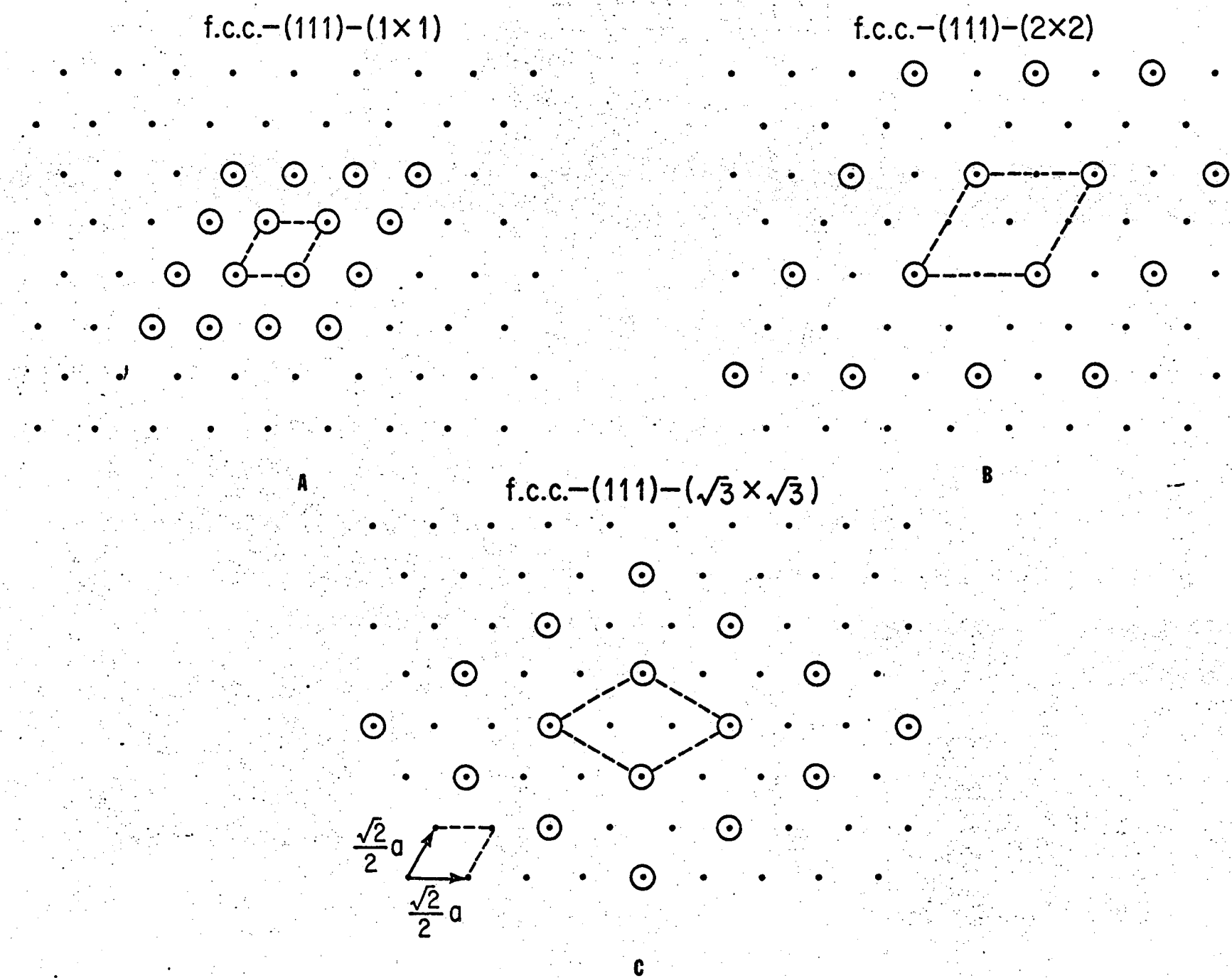


Fig. 1

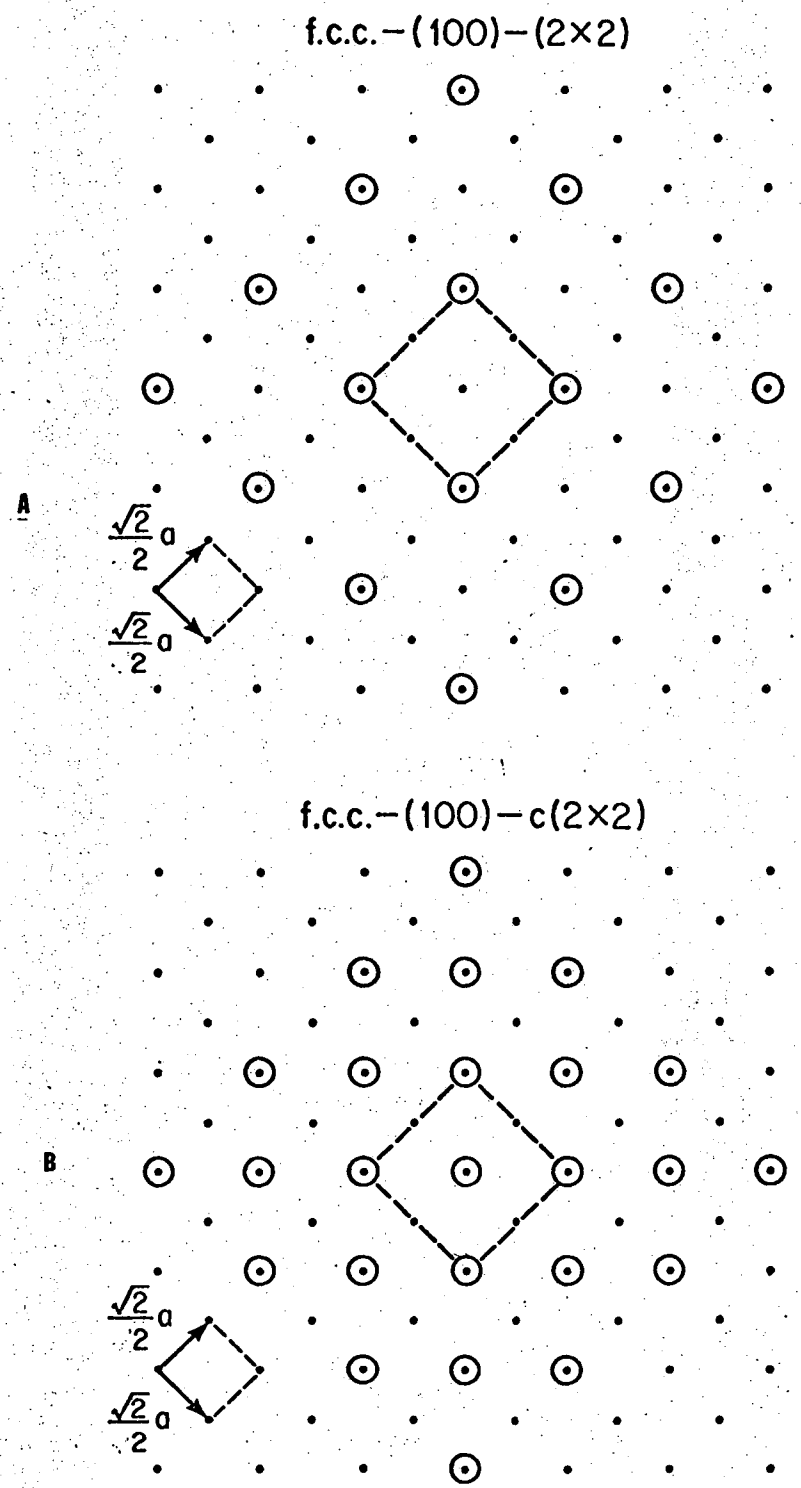
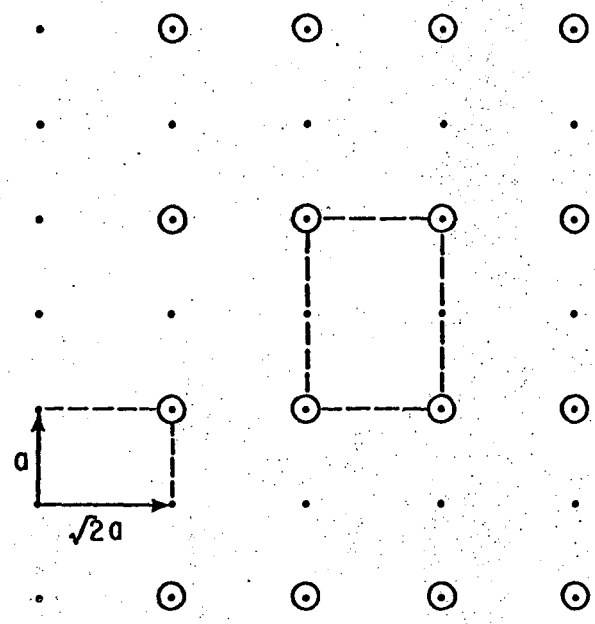

f.c.c.-(100)-(2×2)
A
$\frac{\sqrt{2}}{2}a$
$\frac{\sqrt{2}}{2}a$
f.c.c.-(100)-c(2×2)
B
$\frac{\sqrt{2}}{2}a$
$\frac{\sqrt{2}}{2}a$

Fig. 2

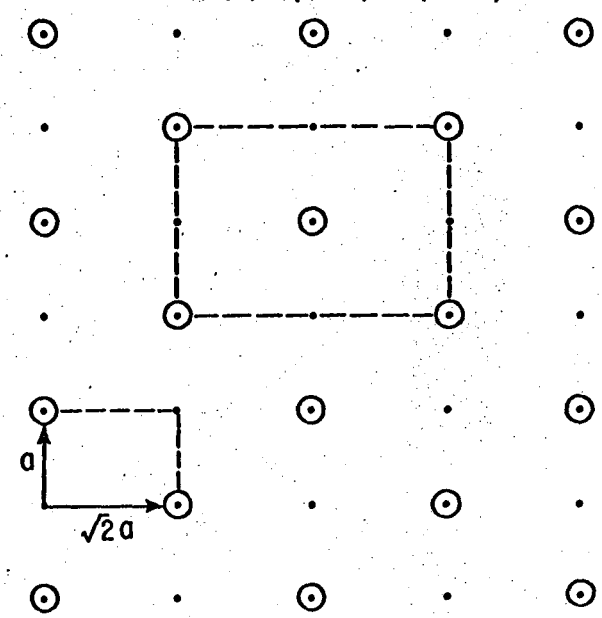
f.c.c.—(110)—(2×2)

A



f.c.c.—(110)—c(2×2)

B



b.c.c.—(110)—(3×1)

C

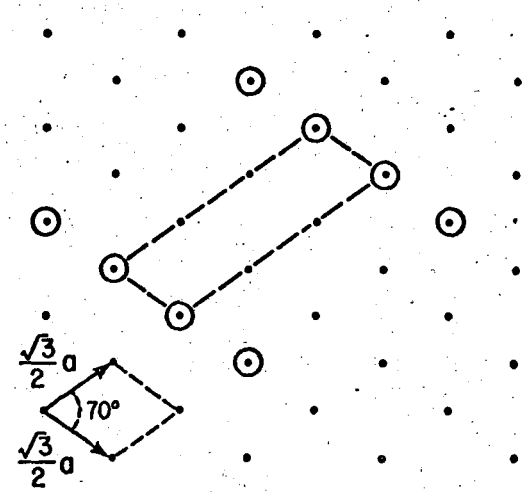


Fig. 3

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