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RECENT PROGRESS IN STRUCTURE DETERMINATION BY LEED

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Surface crystallography with low—energy electron diffraction (LEED) is shown to be developing fast towards solving more complex and diverse kinds of surfaces. This progress is exemplified here with solved structures in three very diverse categories: 1) metal surface reconstructions with multi—layer relaxations; 2) coadsorption of different molecules on metal surfaces; and 3) incommensurate overlayers of graphite on Pt(111).

1. Introduction

Surface structures have been analyzed by low—energy electron diffraction (LEED) for over 15 years [1]. Perhaps 200 structures have been determined by now with this technique. A number of other techniques of surface crystallography have contributed some 50 structures (which in part overlap with the 200 LEED structures). These numbers only count "complete" structural determinations in the sense that the three coordinates of the atoms are known. A recent database, called "Surface Crystallographic Information Service", brings these structures together in a single format [2].

The current trend in LEED is towards more complicated surface structures. Structures with larger two—dimensional unit cells and larger numbers of atoms in each unit cell are being investigated. In addition, surface crystallography by LEED is moving in the direction of disordered structures and incommensurate structures. An imminent advance is also the investigation of stepped surfaces with wide terraces. These developments have been made possible by a number of new techniques introduced in LEED theory in recent years. Their

contribution has been to drastically reduce the computational cost that otherwise arises for complex structures. This is achieved by carefully selecting the dominant multiple–scattering paths and ignoring others. A review of these developments can be found in the literature [3].

In this paper, we shall review a few of the recently determined surface structures. Three categories of structures will be selected to illustrate the diversity of the LEED method. First, a few clean metal surface reconstructions will be discussed, focusing on the missing–row reconstructions of the Ir, Pt and Au(110)–(1x2) surfaces. Here, many structural parameters need to be determined down to several atomic layers below the surface. Then, coadsorption of different molecules on a metal substrate will be presented. This will illustrate complex overlayers with large unit cells and many atoms per unit cell. Finally, an incommensurate structure will be reported: that of graphite formed on Pt(111).

2. Surface reconstructions: fcc(110)–(1x2)

For many years it has been suspected that the (1x2) reconstruction observed on Ir, Pt and Au(110) surfaces could be of the "missing–row" type, which is illustrated in Figure 1. An early LEED analysis [4] confirmed this model for Ir, but similar analyses of Pt [5] and Au(110)–(1x2) [6] were not so succesful. The doubts about the missing–row model were removed by other types of experiments (especially scanning tunneling microscopy [7] and x–ray diffraction [8]). New LEED analyses then confirmed the missing–row model also for the Au [9] and Pt [10] structures, but only after inclusion of relaxations in deeper layers. Such relaxations were less strong in Ir, but were also detected there [11]. The results for the three metals are quantified in Table 1.

3. Coadsorption of molecules on metal surfaces

A number of different molecules (and one type of atom) were coadsorbed on the (111) faces of Rh, Pt and Pd: they are CO, NO, C_2H_2, C_2H_3, C_6H_6 and Na [12]. The ethylidyne, C_2H_3, is obtained from hydrogenation of acetylene, C_2H_2, or from dehydrogenation of ethylene, C_2H_4.

An unexpected trend emerged regarding which pairs of these adsorbates form long–range ordered structures. Let us split these adsorbates in two groups: CO and NO, on the one hand, which we shall call electron acceptors, and C_2H_2, C_2H_3, C_6H_6 and Na on the other hand, which we shall call electron donors. The acceptor and donor labeling is based on the sign of the work function change measured upon adsorption. Then, it is found [12] that mixing acceptors with

donors produces well-ordered structures, while mixing acceptors with acceptors or donors with donors does not. It appears that acceptors like to surround themselves with donors and vice versa. This generally produces more stable ordering then do the pure (unmixed) overlayers. For example, overlayers of pure benzene, C_6H_6, are either weakly ordered or are not ordered, while CO coadsorbed with benzene forms very stable ordered lattices. Figure 2 illustrates the case of benzene coadsorbed with CO on Pd(111) [13], while Figure 3 shows NO and ethylidyne coadsorbed on Rh(111) [14].

4. Graphite on Pt(111)

Graphite is easily formed on many metal surfaces by thermal decomposition of hydrocarbons. It is also easily recognized by its characteristic LEED pattern. However, little is known about the actual bonding geometry of such graphite layers on the metal substrate. Only their two-dimensional lattice constant is easily obtained and it is found to be generally incommensurate with the substrate lattice constant.

A LEED theory has been developed for this situation, while LEED intensities were measured for graphite on Pt(111) [15]. The resulting structure is illustrated in Figure 4. A single graphite sheet lies parallel to the surface, but it is supported by individual carbon atoms chemisorbed in hollow sites of the Pt(111) substrate. This surface undoubtedly also contains a variety of other carbon species, such as small tilted pieces of graphite and interstitial carbon below the surface. These would not contribute substantially to the LEED intensities and are then filtered out of consideration by the LEED analysis.

5. Conclusions

Present theoretical and experimental techniques in LEED now make it possible to determine structures of increasing complexity and variety. New techniques are now being developed to extend surface crystallography to disordered surfaces [16,17] and stepped [18] surfaces, including defects [19], impurities and adsorbates near such irregularities. For instance, the bonding structure of disordered oxygen on W(100) has already been analyzed in detail, showing an adsorbate-induced distortion of the substrate [17].

The only major remaining barrier to structural determination of complex surfaces is the issue of how to search through the high-dimensional structural parameter space for the correct solution. This is the same issue facing x-ray crystallography. There are no universal mathematical methods that are effective at finding the correct structural solution in a unique

and reliable manner in a high–dimensional parameter space.

On the experimental side, automated data acquisition systems are already available to handle the demand for larger data bases to solve more complex structures. Diffuse intensities due to disordered surfaces can also be measured, either with a video camera [20] or, better, with a position–sensitive detector [21].

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Figure Captions

Figure 1. Structural diagram of reconstructed fcc(110)–(1x2), representative of the corresponding Ir, Pt and Au surface structures. Specific values for the various structural parameters are listed in Table 1

Figure 2. Side view (top panel) and top view (main panel) of Pd(111)–(3x3)–C_6H_6+2CO. Van der Waals contours are given for the molecules. The hydrogen positions are assumed. A (3x3) unit is outlined. Selected distances are shown, indicating a C_6 ring distortion relative to the gas–phase C_6H_6 molecule (for which the C–C distances are all 1.397Å)
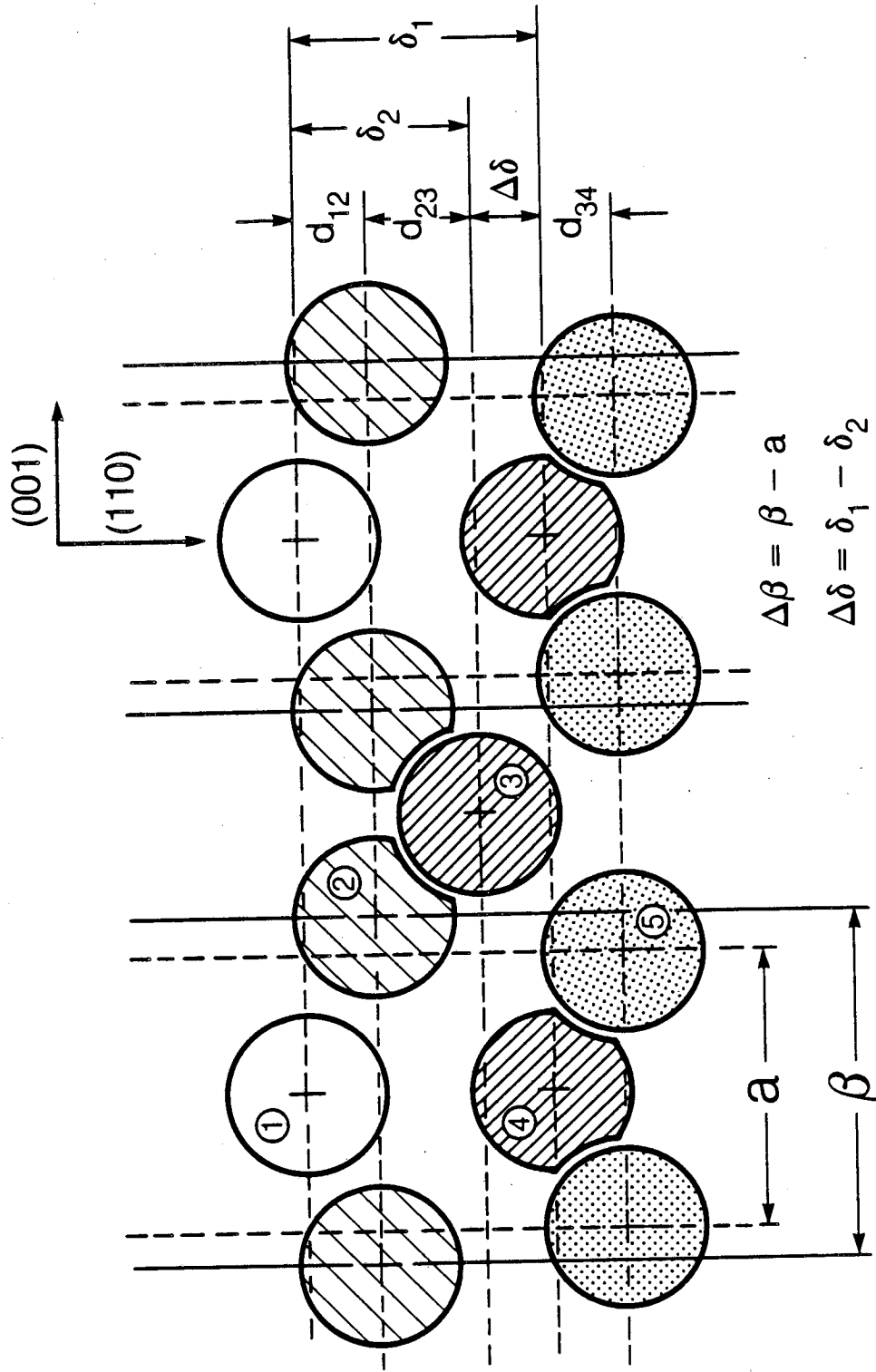
Figure 3. A coadsorption structure of NO and ethylidyne on Rh(111). Both types of molecules have their axes perpendicular to the surface and occupy inequivalent types of three–fold hollow sites (the hydrogen positions are guessed)

Figure 4. Structural diagram of a graphite layer adsorbed on Pt(111), with an intercalated chemisorbed carbon layer. The graphite layer is incommensurate with the substrate, while the individual carbon atoms are bonded in hollow sites of the substrate

Table 1. Geometries of Missing–Row Reconstructions on fcc(110) Surfaces, as obtained by LEED (for notation, see Figure 1).
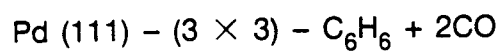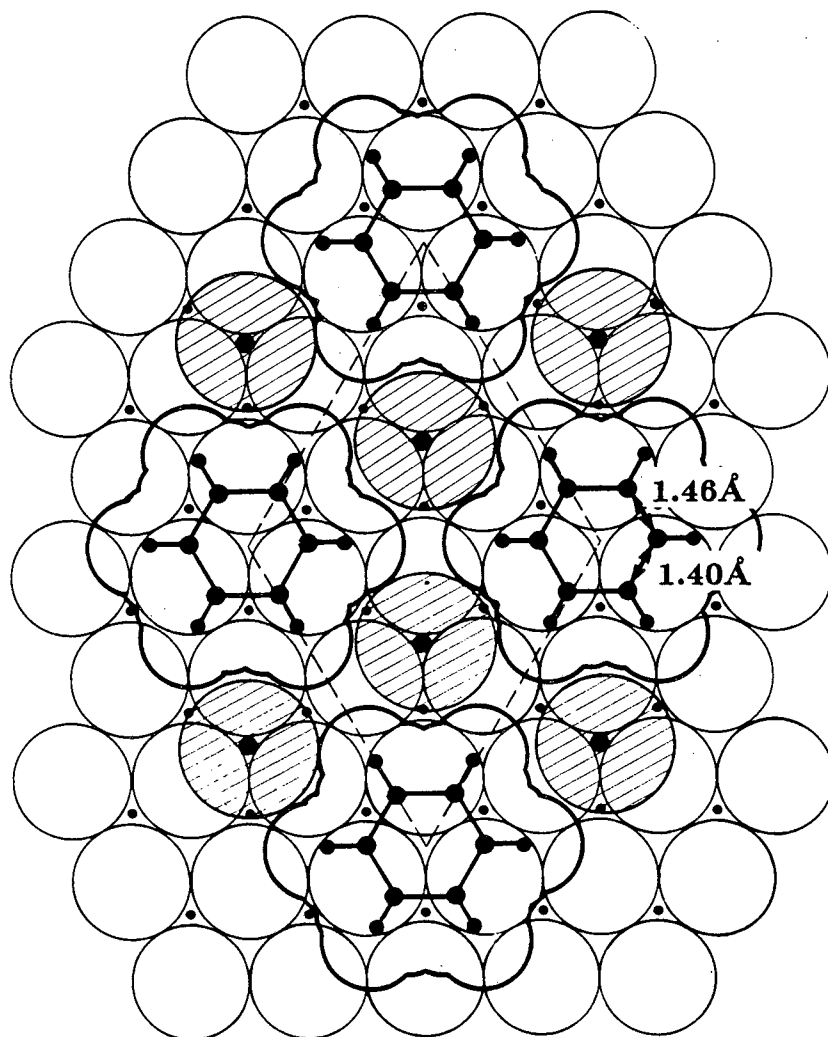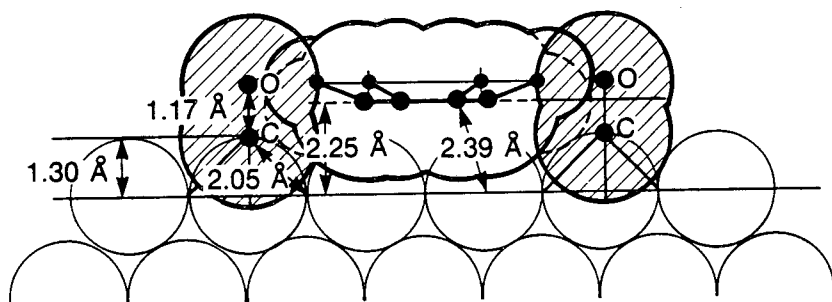
110 Surface	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}	$\Delta \delta_3$	$\Delta \beta_2$	$\Delta \beta_4$
Ir	-0.17	-0.16	-0.08	—	0.23	0.07	—
Pt	-0.26	-0.18	-0.12	-0.01	0.32	0.13	0.24
Au	-0.29	0.03	0.03	—	0.24	0.14	—

fcc (110) – (1 × 2) missing-row model

(001)
(110)

δ_1
δ_2
$\Delta\delta$

d_{12}
d_{23}
d_{34}

$\Delta\beta = \beta - a$
$\Delta\delta = \delta_1 - \delta_2$

a
β

XBL 857-11651

Fig. 1

9

Pd (111) – (3 × 3) – C$_6$H$_6$ + 2CO

XBL 872-9565

Fig. 2

10

Rh(111) + c(4×2) NO + Ethylidyne(CCH$_3$)

Fig. 3

11
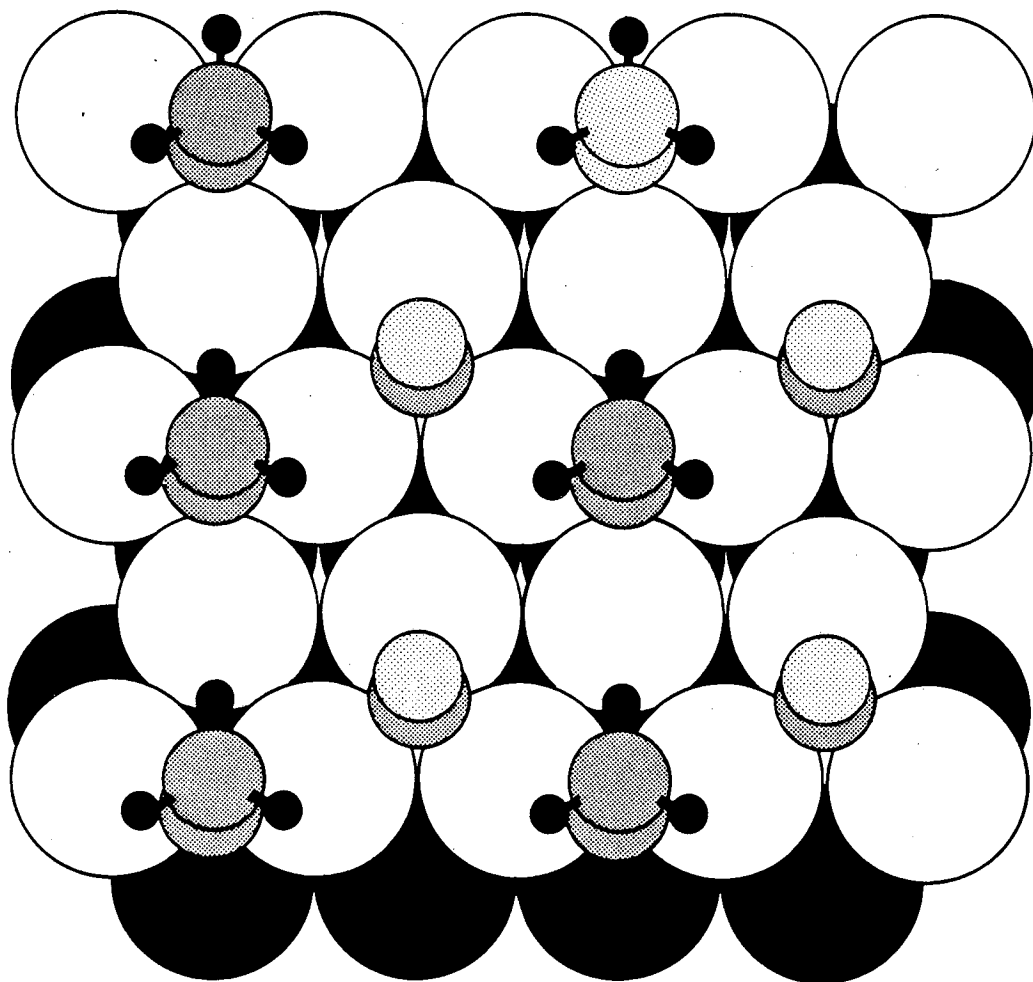
Incommensurate graphite
on Pt (111)
with C intercalate

Graphite

C intercalate

Pt (111)

4.26 Å

1.42 Å

2.78 Å

2.45 Å

3.70 Å

1.25 Å

XBL 8512-12785

Fig. 4

12