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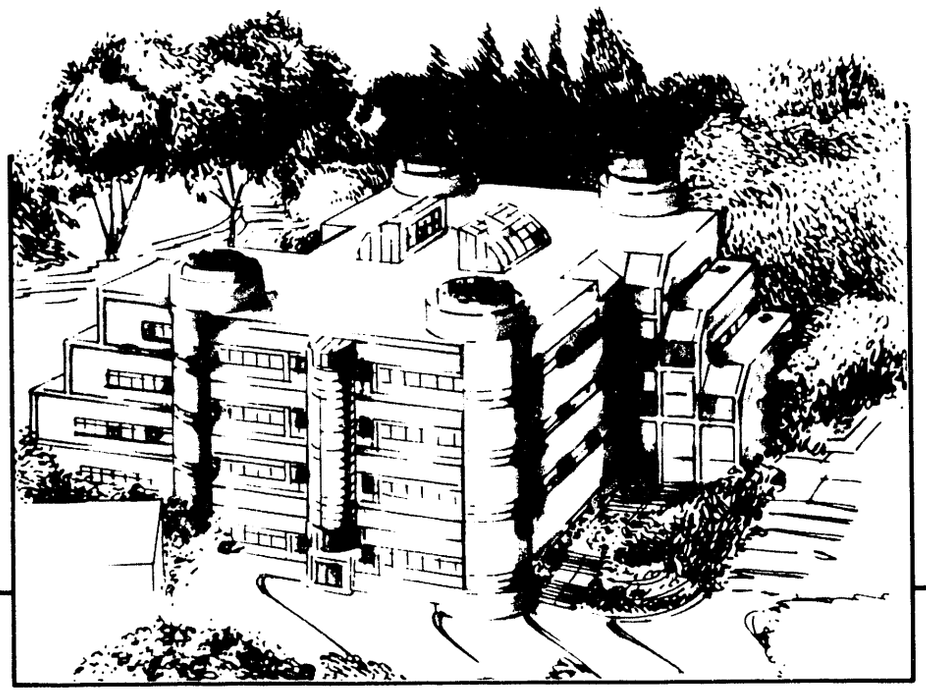
## The Puzzles of Surface Science and Recent Attempts to Explain Them

G.A. Somorjai

July 1990



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# The Puzzles of Surface Science and Recent Attempts to Explain Them

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# Abstract

Surfaces have several unique properties that remain unexplained on the atomic level. These include 1) the unique chemical activity of rough surfaces, 2) the breaking of chemical bonds in narrow temperature ranges; and 3) the role of co-adsorption and strongly adsorbed monolayers during catalysis and tribological change (friction, lubrication). The dynamic surface restructuring model and surface structure induced variations in local density of states that have been suggested to rationalize the surface behavior await experimental confirmation.

# Introduction

Modern surface science is capable of investigating the surface monolayer on the atomic scale[1]. Low energy electron diffraction (LEED), the scanning tunneling microscope (STM) and electron microscopies provide surface structure while x-ray photoelectron and Auger electron spectroscopies (XPS and AES), ion scattering and secondary ion mass spectroscopies (ISS and SIMS) yield surface composition and surface atom oxidation states[2]. High resolution electron energy loss spectroscopy (HREELS), Fourier transform infrared (FTIR), and Sum Frequency Generation (SFG) provide orientation and location of adsorbed molecules through vibrational spectroscopy. All these molecular level properties can be related to macroscopic surface phenomena that include chemisorption, surface diffusion, catalytic reaction rates and product distribution, friction and lubrication. These combined molecular level and macroscopic surface studies focused attention on several unique surface properties that remain unexplained on the molecular level. These I call the puzzles of surface science. In this paper I would like to discuss three of these; 1) The unique chemical activity of rough surfaces; 2) The breaking of chemical bonds in narrow temperature ranges; and 3) The role of co-adsorption and strongly adsorbed monolayers during catalysis and tribological change (friction, lubrication).

A good atomic model of the solid surface should explain all these phenomena. At present no such model exist. It appears that the more classical static models are unable to provide rational explanations for these experimental findings and that the dynamic restructuring of surfaces has to be invoked that occurs in response to the changing surface chemical environment.

The purpose of this paper is to review three surface phenomena that were uncovered by investigations over the past two decades along with the development of atomic models that were proposed to explain them. Our present state of understanding is exposed and experimental studies are suggested in order to better correlate the proposed models and the data.

## 1. The Unique Chemical Activity of Rough, Surfaces

Thermal desorption studies indicate that the chemisorption bonds of adsorbed atoms and molecules are stronger at surface defect sites, at steps and kinks, than on flat, close-packed smooth surfaces[1]. The maximum rates of desorption shift to higher temperatures for species adsorbed at these more open surface sites. This is shown for CO chemisorbed at the platinum stepped (533) crystal face and for hydrogen adsorbed on the flat (111), stepped (557) and kinked (12,9,8) platinum surfaces (Figures 1a and 1b)[1]. Another example is the thermal decomposition of ethylene[3] on the nickel (111), (110) and stepped

5(111)x(110) crystal faces (Figure 2). Bond breaking shifts to much lower temperature, <150K, at the step sites. Molecular beam scattering studies of $H_2/D_2$ exchange[4] clearly show that at low coverages the dissociation probability of $H_2$ at defect sites steps is near unity while flat, defect free (111) platinum surfaces have dissociation probability of less than $10^{-3}$, (Table 1)[5].

## 2. Breaking of Chemical Bonds in Narrow Temperature Ranges

At low enough temperatures adsorbed molecules remain intact even on the most reactive metal surface. Thermal activation is necessary for bond breaking. There are narrow, well defined temperature ranges for the bond breaking for a given adsorbate-substrate system, and for polyatomic molecules the bond scission is sequential, not all molecular chemical bonds break at the same temperature. A typical bond breaking sequence is shown for light alkenes[6] on the platinum (111) crystal face (Figure 3). Hydrogen evolution occurs at maximum rates at well-characterized temperatures leaving a partially dehydrogenated stable organic fragment on the surface[7]. The type of species that form are shown for chemisorbed ethylene in Figure 4. The temperature at which molecular bond breaking occurs shifts to lower temperatures for rough surfaces as shown in Figure 2. There are many examples of thermal activation and sequential bond breaking for molecules ranging from $N_2$ to pyridine[8] on transition metal surfaces including iron, rhodium[9] and platinum.

## 3. The Role of Co-Adsorption and Strongly Adsorbed Monolayers During Catalysis and Tribological Change (Friction, Lubrication).

High coverages of chemisorbed molecules exhibit decreasing integral heats of adsorption indicating the weakening of the average adsorbate-substrate bonds. This effect is due to the repulsive adsorbate-adsorbate interaction that often forces the molecules onto new adsorption sites[10]. The co-adsorption of two different molecules, one acceptor, the other a donor to the metal substrate, leads to ordering into a mixed layer due to attractive adsorbate-adsorbate interactions. One example of this is the surface structure that forms upon the coadsorption of CO and ethylene, shown in Figure 5. The co-adsorption of two donors or two acceptors yield disordered monolayers as indicated by the various examples in Table 2[11].

However, there are many examples indicating that one of the chemisorbed species during co-adsorption can also restructure the substrate. Chemisorbed potassium restructures[12] iron oxide (Figure 6), oxygen or alumina restructure[13] iron (Figure 7), sulfur or carbon restructure nickel[14] and rhenium (Figure 8)[15]. Thus, the chemisorbed, co-adsorbed species exert their chemical influence not only by altering the adsorbate-adsorbate bond but also through restructuring the substrate. This effect is particularly

noticeable during catalytic reactions[16]. In this circumstance, strongly chemisorbed species; organic fragments, alkali or halide ions, sulfur, carbon or oxygen exert their promotional effects as substrate structure and bonding modifiers by altering the clean substrate structure. Frequently when both co-adsorbed species chemisorb and desorb periodically, the surface structure also changes periodically, often with the period of the turnover frequency of the catalytic reaction.

A monolayer of strongly chemisorbed atoms (sulfur for example) can also act as a lubricant, markedly decreasing the friction coefficient of the surface. This is surprising since the load applied is usually so large that macroscopic indentation is expected. In this circumstance, a monolayer of adsorbed atoms are not likely to inhibit the massive fracture of chemical bonds penetrating over hundreds of atomic layers. Nevertheless, experiments indicate large changes in lubricity upon introduction of an adsorbed monolayer. We shall invoke chemisorption induced restructuring later in this paper to rationalize this observation.

## Historical Development of Models of Surfaces.

The first model utilized to explain various surface phenomena represented the surface as a smooth, structureless discontinuity (Figure 9). Developed in the 1930's, it was

used to explain adsorption isotherms, the presence of surface space charge at electrode and colloid surfaces, and changes of work function from crystal face to crystal face and upon adsorption[1]. The rough surface-rigid lattice model was developed next, in the 1950's (Figure 10). This model was successful in explaining the presence of surface defects, steps and kinks, that could be detected by electron and field ion microscopies[1]. Theories of macroscopic crystal growth, evaporation and surface atom transport (diffusion) that utilized this model yielded good agreement with experimental data. It should be noted that the rigid lattice approximation could be used to predict the location of surface atoms from the projection of the bulk unit cell to that surface. It was assumed that during chemisorption or other surface chemical change the substrate atoms maintain their equilibrium positions they occupied in their clean state. This simplifying assumption could not be readily confirmed by experiments as most surface science techniques were sensitive to the location of atoms or molecules in the topmost layer and the location of the substrate atoms buried under the chemisorbed layer could not be detected.

In recent years there is growing evidence that the substrate surface restructures during chemisorption or other chemical change[15]. Low energy electron diffraction (LEED)

surface crystallography studies are capable of determining the locations of atoms and molecules in the top three layers near the surface. The surface atoms "relax" inward when clean and the magnitude of relaxation increases with roughness (defined as the reciprocal of the packing density). Large changes in equilibrium positions lead to reconstruction whereby surface atoms order into new structures with different surface unit cells to maximize their bonding at the anisotropic surface sites. Chemisorption induces further restructuring in the substrate layer whereby atoms move outward, rotate, move towards or away from the chemisorbed species near the chemisorption site[15]. All these restructuring processes occur to optimize the magnitude of the surface chemical bonds and thus, the type of restructuring that occurs depends on the adsorbate-substrate interaction and also influenced by the interaction among adsorbate molecules (coverage and co-adsorption effects). Chemisorption induced restructuring occurs because the adsorbate-substrate bonds are of the same magnitude as the strengths of the substrate-substrate bonds. They take place on the time scale of chemisorption and are often reversed when desorption commences. That is, adsorption induced restructuring is a dynamic phenomenon. Surface restructuring can be induced by other surface chemical changes that include the turnover of catalytic

reactions, oxidation or reduction, sintering or redispersion of particles. In these circumstances, the time periods needed for restructuring are longer than chemisorption or desorption times and often controlled by surface atom diffusion; mass transport[15]. There are examples for these changes from recent studies of CO oxidation over single crystal surfaces[17] and[18] electron microscopy studies of sintering and redispersion of metal particles.

Let us now discuss how we might explain the three chemical surface phenomena described above in light of the various surface models, especially the dynamic adsorption induced restructuring model of surfaces and interfaces.

**(i) Why rough surfaces are more reactive in chemical bond breaking and for catalysis.**

The large relaxation of atoms at open, low packing density surfaces[19] and at defect sites (steps, and kinks) when clean provide for large amplitude movement upon chemisorption to new equilibrium positions. The change in site symmetry permits the adsorbing molecules to optimize bond strength to the substrate or to dissociate (atomize diatomic molecules, $H_2$ or $N_2$, for example).

The same strong chemisorption site cannot be active in catalytic turnover as well. High heat of adsorption implies long residence times at the adsorption sites yet, rough surfaces and defect sites also exhibit high turnover rate

(implying short surface residence times) for catalytic reactions. This puzzle or apparent contradiction can be explained assuming that two different sites are involved; one for strong chemisorption and another for high turnover reaction. Indeed we suggested, using the rigid lattice model that the top atoms at a step are sites of strong chemisorption bond formation and the bottom of the step is the catalytic site[20]. Although this model may be reasonable for explaining strong hydrogen chemisorption and simultaneous rapid $H_2/D_2$ exchange at stepped metal surfaces the chemisorption of larger atoms (nitrogen, for example) would block neighboring reaction sites. A more likely explanation is that strong chemisorption restructures the surface thereby creating new sites where the catalytic reaction occurs. The concept that the catalytically active site does not exist on the clean surface prior to strong chemisorption of some of the reactants is a powerful one. However, it needs experimental confirmation using techniques that are sensitive to the location of both the adsorbed and the substrate atoms and to the change of location on time scales that are shorter than reaction turnover times. Perhaps, scanning tunneling microscopy (STM) studies under reaction conditions will permit experimental verification of this explanation based on the dynamic chemisorption induced surface restructuring model.

The coverage dependence of the dissociation probability has been observed for many chemisorption systems. In some cases the sticking probability (associated with dissociation of a diatomic molecule, for example) decreases with increasing coverage[21] in other cases it is increasing with increasing coverage[22]. Since surface restructuring is also likely to be dependent on coverage it would be important to search for experimental verification for the correlation between changes of dissociation probability and restructuring with coverage.

**(ii) Thermal activation of chemical bond breaking.**

This process occurs at specific narrow temperature ranges for a given adsorbate-substrate system; markedly lower temperatures on rough surfaces and bonds break in sequence, not all of them at the same temperature. While activated chemisorption has been described using the rigid lattice model[1], surface restructuring would permit the greater diversity of rough surface and sequential bond breaking behavior.

**(iii) The co-adsorption bond is usually described as primarily due to adsorbate-adsorbate interactions, direct or through the metal substrate (bonding modifier[23]).** Nevertheless, adsorbate induced restructuring is well documented in the case of chemisorbed alkali metal ions,

oxygen, sulfur and carbon. Thus, if one of these species co-adsorb it may also exert chemical influence by changing the substrate structure to one that is more reactive (structural promotion) or less reactive (reaction poison or inhibitor[24]). It is likely that both these effects operate simultaneously for most coadsorbed systems. Restructuring could be invoked also to explain changes of lubricity by a strongly chemisorbed monolayer. The restructured surface can be elastically deformed over a larger range of applied load, thereby increasing the contact area between the load and the surface. Since the pressure is the load over the area a reduction of local pressure decreases the friction coefficient and helps lubrication.

## Acknowledgement

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# Figure Captions

Figure 1: Thermal desorption of A) CO from the stepped platinum (533) face as a function of coverage and B) $H_2$ from the flat (111), stepped (557) and kinked (12, 9, 8) platinum surfaces.

Figure 2: Thermal decomposition of ethylene on the flat Ni(111), Ni(110) and stepped Ni 5(111)x(110) surfaces.

Figure 3: Sequential dehydrogenation of several alkenes with increasing temperature on Pt(111).

Figure 4: The surface species that form upon the sequential dehydrogenation of ethylene on Rh(111).

Figure 5: The co-adsorbed CO and ethylene surface structure on Rh(111).

Figure 6: Potassium induced restructuring of iron oxide.

Figure 7: Alumina induced restructuring of iron.

Figure 8: Carbon chemisorption induced restructuring of the nickel (100) crystal face.

Figure 9: The smooth, structureless surface model.

Figure 10: The rough, rigid lattice surface model.

# Table Captions

Table I. Structure sensitivity of $H_2/D_2$ Exchange at Low Pressures ($\sim 10^{-6}$ torr).

Table II Ordered and disordered co-adsorbed layers. Acceptor-donor coadsorbed molecules order, acceptor-acceptor, donor-donor coadsorbed monolayers disorder.

# TABLE I

**Structure sensitivity of $H_2/D_2$ Exchange at Low Pressures ($\sim 10^{-6}$ torr).**

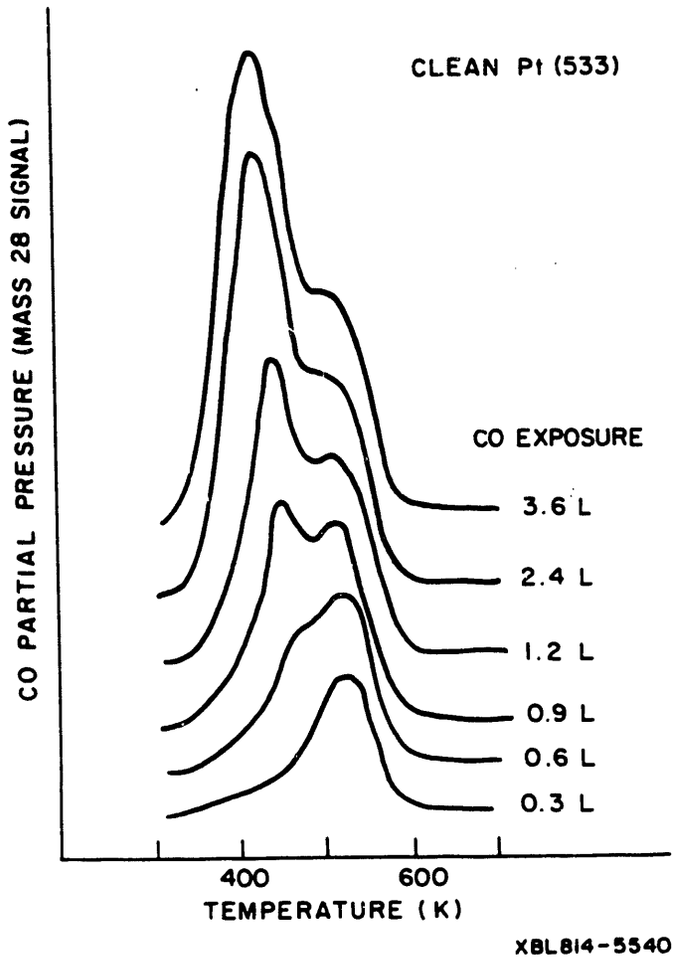
| | reaction probability |
|---|---|
| Stepped Pt(332) | 0.9 |
| Flat Pt(111) | $\sim 10^{-1}$ |
| "Defect free" Pt(111) | $\leq 10^{-3}$ |

# TABLE II

**Ordered and disordered co-adsorbed layers. Acceptor-donor coadsorbed molecules order, acceptor-acceptor, donor-donor coadsorbed monolayers disorder.**

| Adsorbates | Ratio | Coadsorbed LEED Pattern |
|---|---|---|
| NO + $\equiv C.CH_3$ | 1:1 | c(4x2) |
| CO + $C_2H_2$ | 1:1 | c(4x2) |
| CO + $\equiv C.CH_3$ | 1:1 | c(4x2) |
| CO + $C_6H_6$ | 2:1 | (3x3) |
| CO + $C_6H_6$ | 1:1 | c(2√3x4) rect |
| CO + $C_6H_5F$ | 2:1 | (3x3) |
| CO + $C_6H_5F$ | 1:1 | c(2√3x4) rect |
| CO + Na | 1:1 | c(4x2) |
| CO + NO | | Disorder |
| Na + $C_2H_2$ | | Disorder |
| Na + $\equiv C.CH_3$ | | Disorder |
| Na + $C_6H_6$ | | Mixed* |

* - 2 patterns characteristic of individual adsorbates observed suggesting phase separation into independent domains.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CO EXPOSURE
3.6 L
2.4 L
1.2 L
0.9 L
0.6 L
0.3 L
400
600
TEMPERATURE (K)
XBL814-5540

Fig. 1A

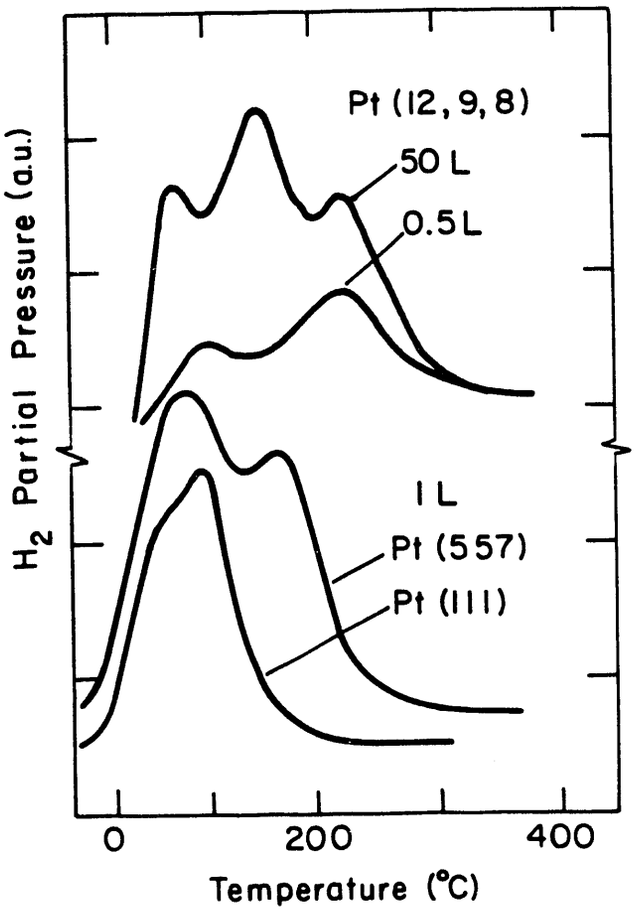


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Fig. 1B

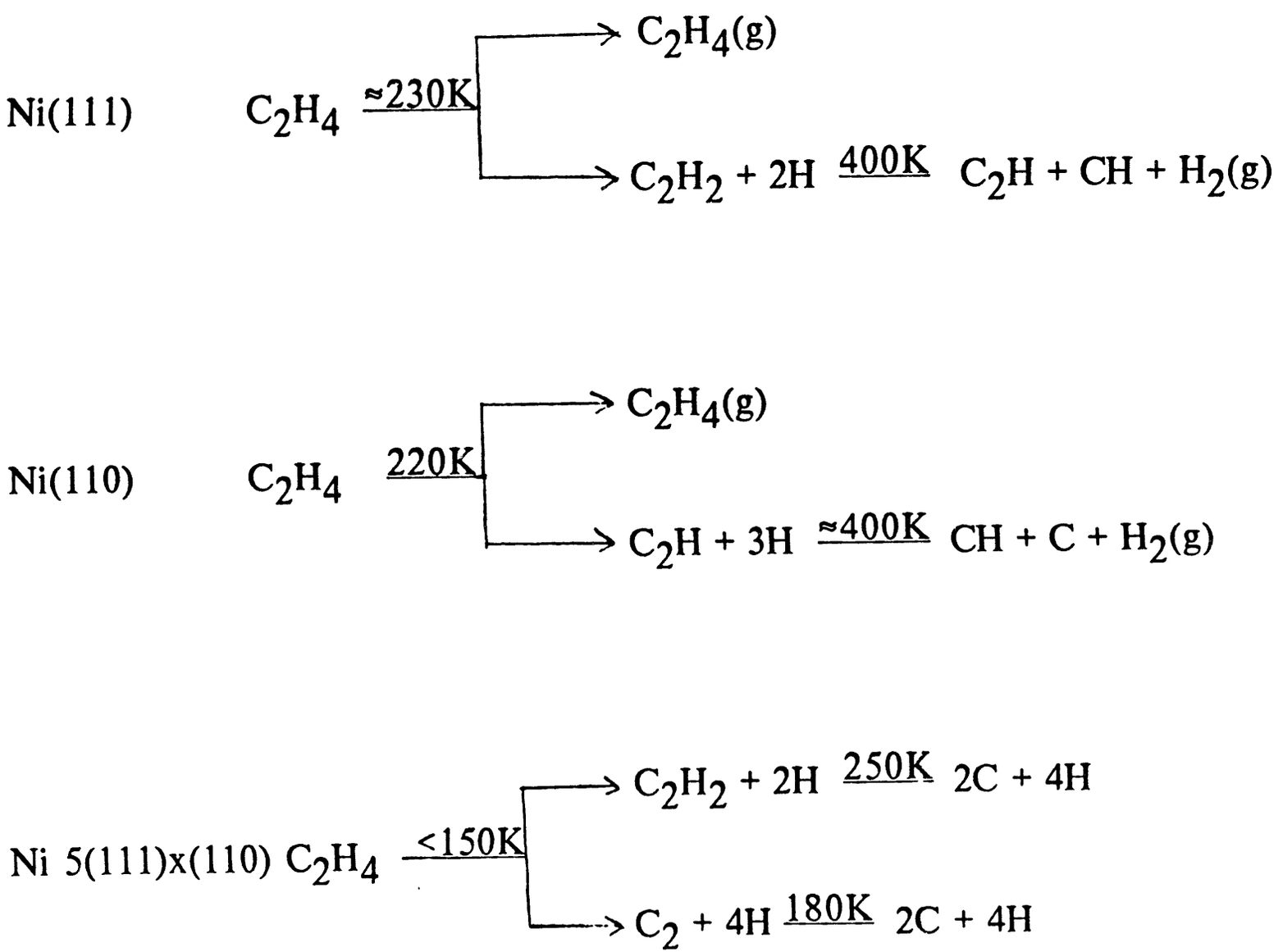

Ni(111)
C2H4
≈230K
C2H4(g)
C2H2 + 2H
400K
C2H + CH + H2(g)
Ni(110)
C2H4
220K
C2H4(g)
C2H + 3H
≈400K
CH + C + H2(g)
Ni 5(111)x(110) C2H4
<150K
C2H2 + 2H
250K
2C + 4H
C2 + 4H
180K
2C + 4H

Fig. 2

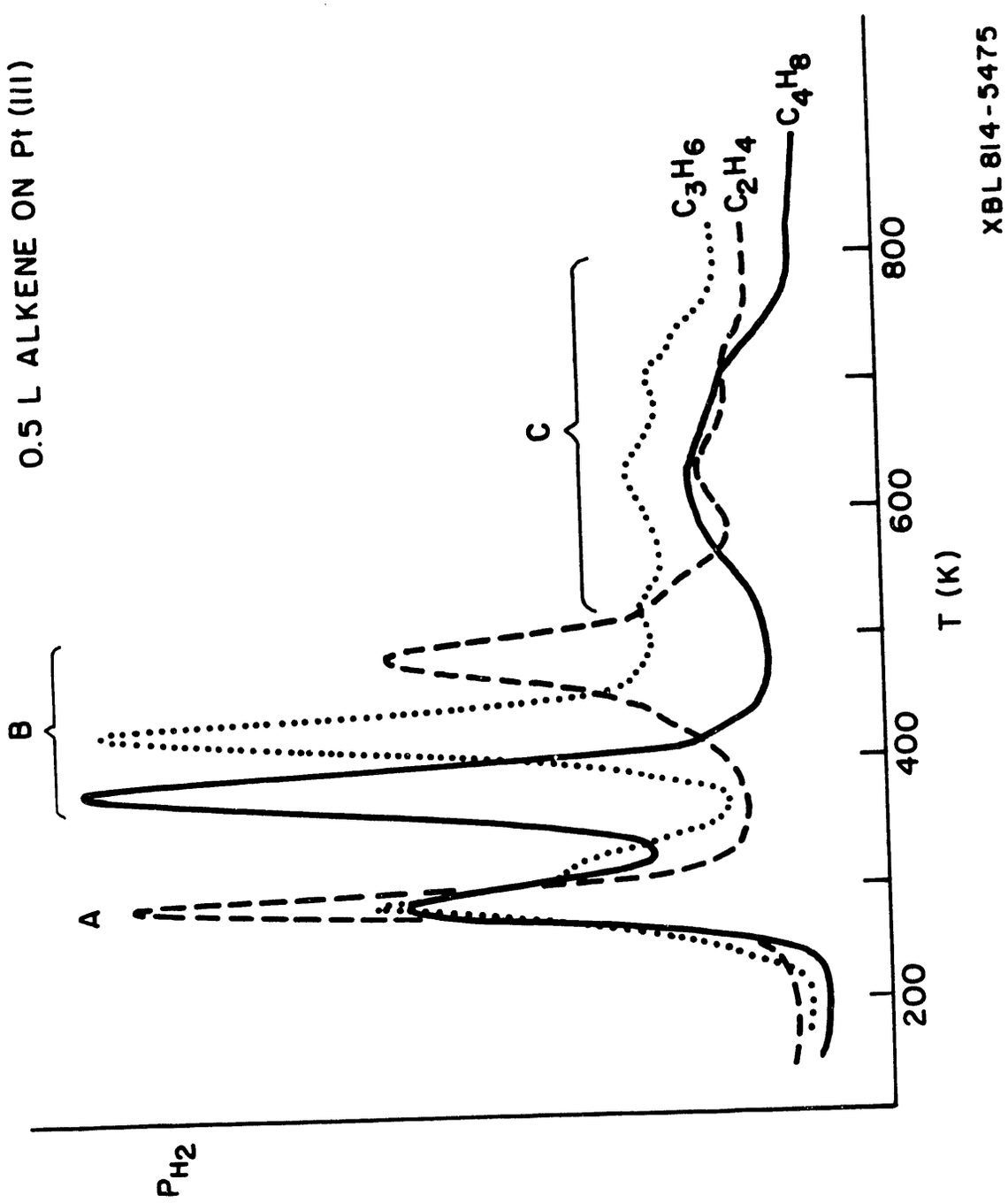
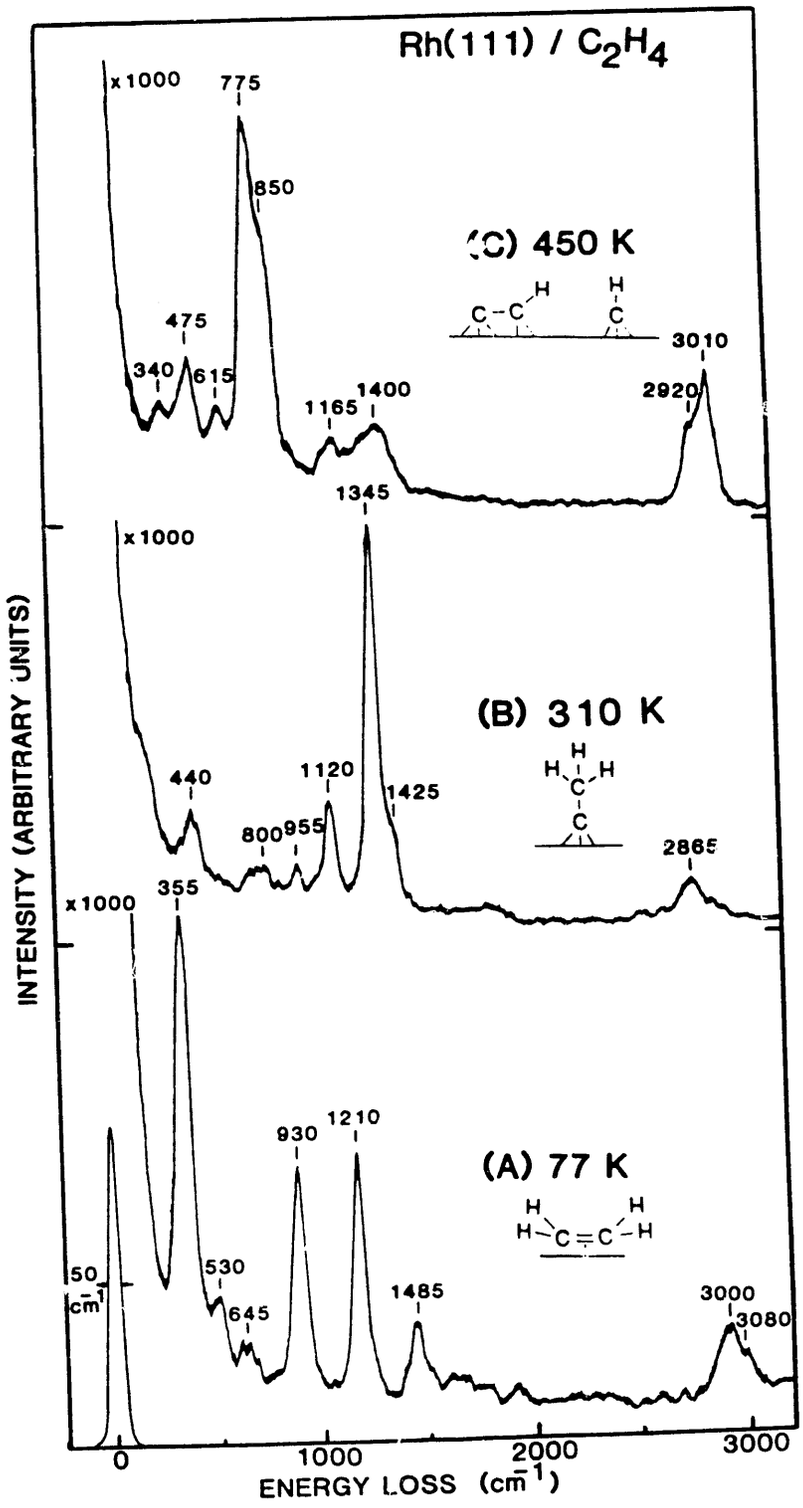
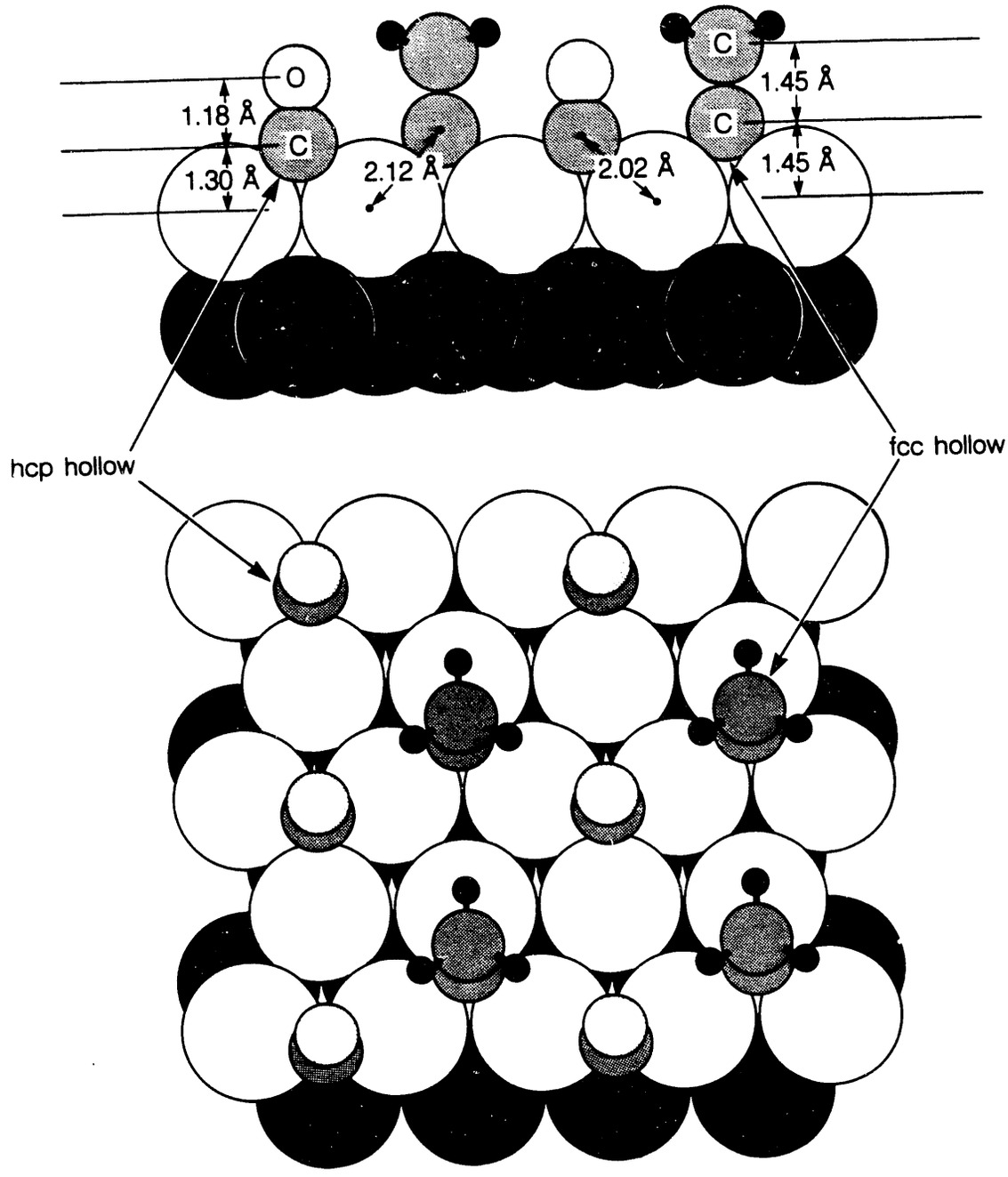

0.5 L ALKENE ON Pt (111)
A
B
C
$C_3H_6$
$C_2H_4$
$C_4H_8$
$P_{H_2}$
200
400
600
800
T (K)
XBL 814-5475

Fig. 3




XBL 8512-4941

Fig. 4




Rh(111) + c(4×2) CO + Ethylidyne($CCH_3$)

XBL 877-7004

Fig. 5

# MODEL FOR ALKALI INDUCED RESTRUCTURING OF 1 ML $FeO_x$/Pt(111)

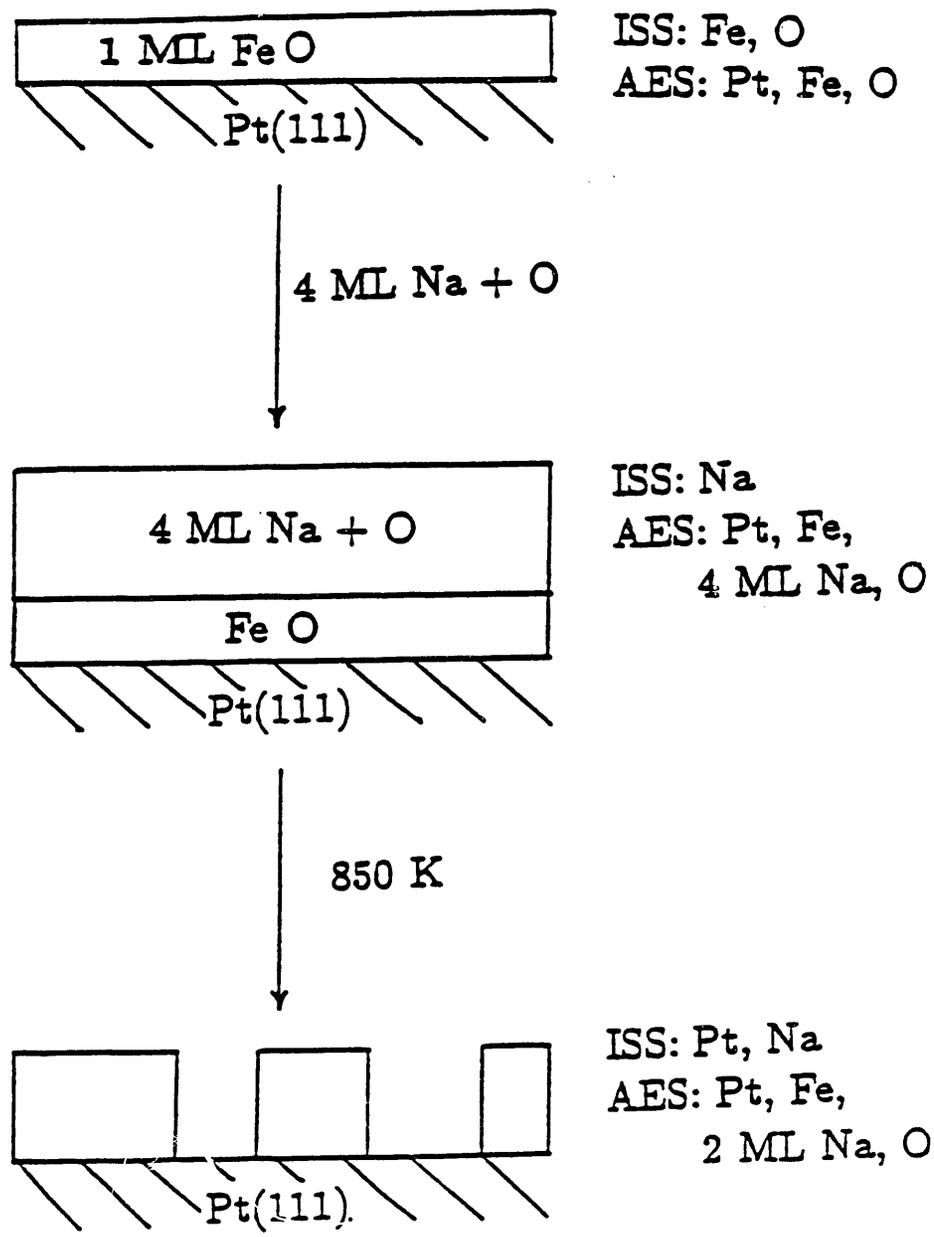



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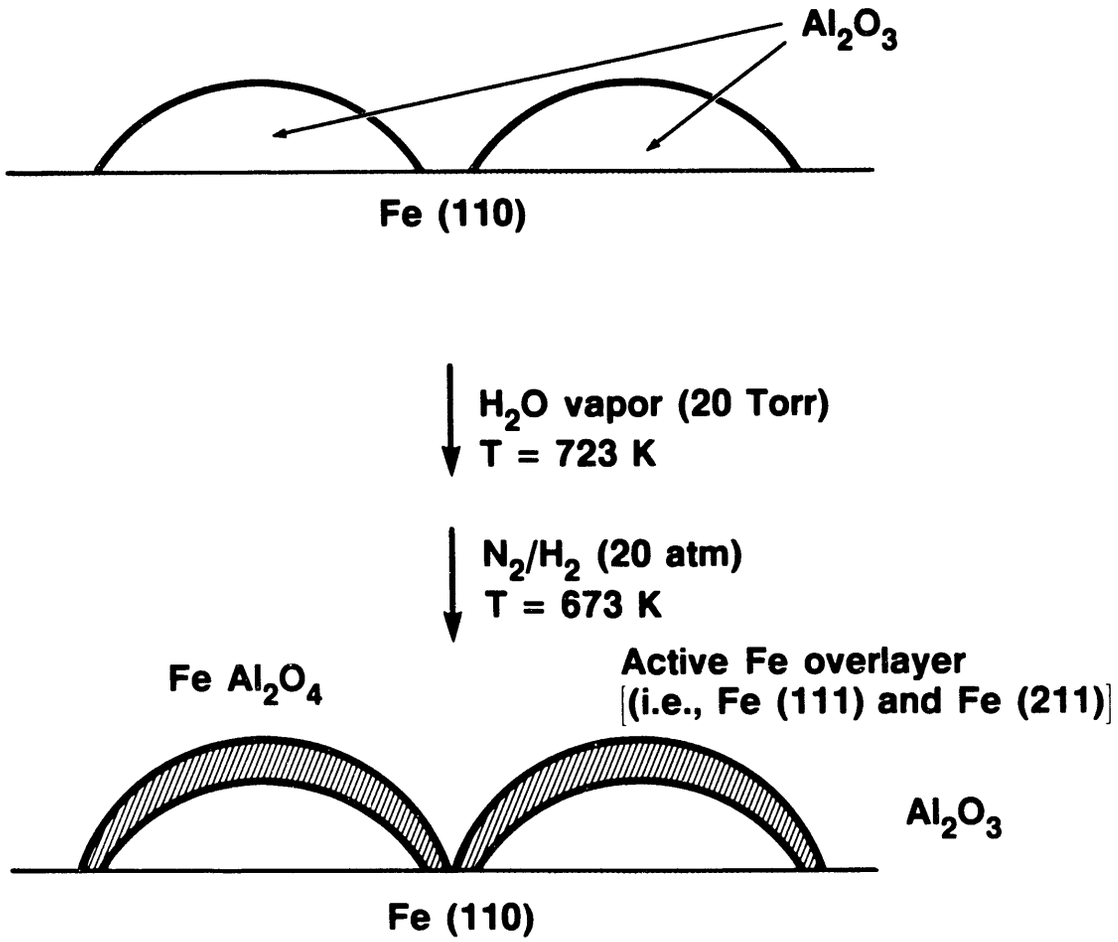
Fig. 6




XBL 871-337

Fig. 7

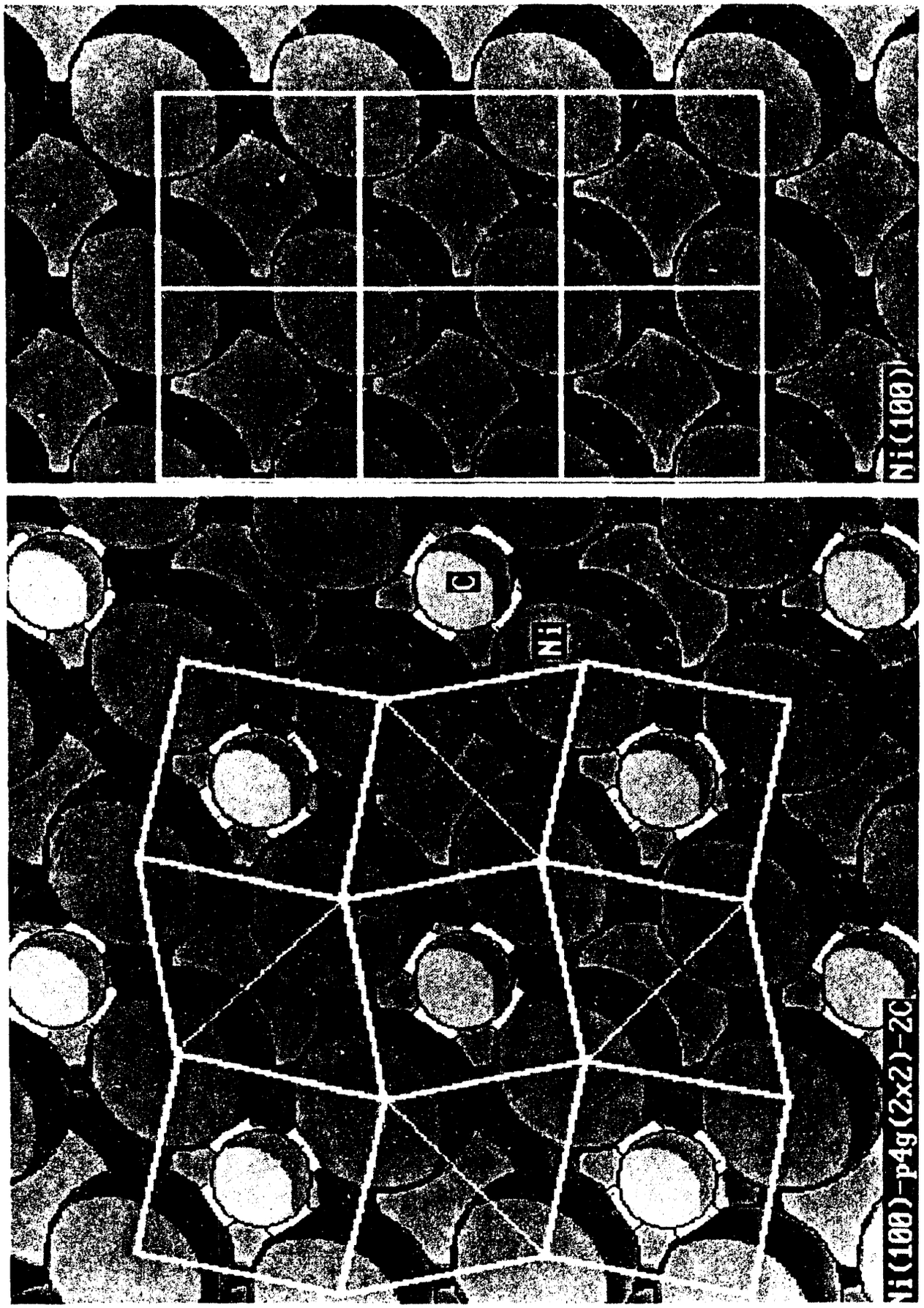



Fig. 8

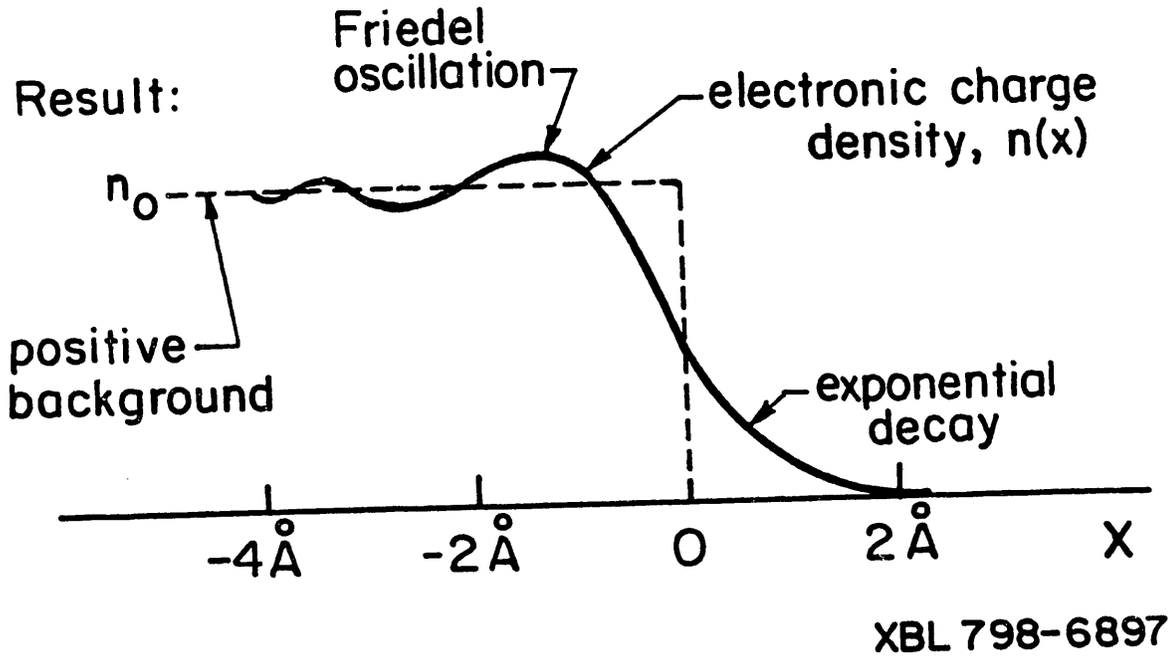
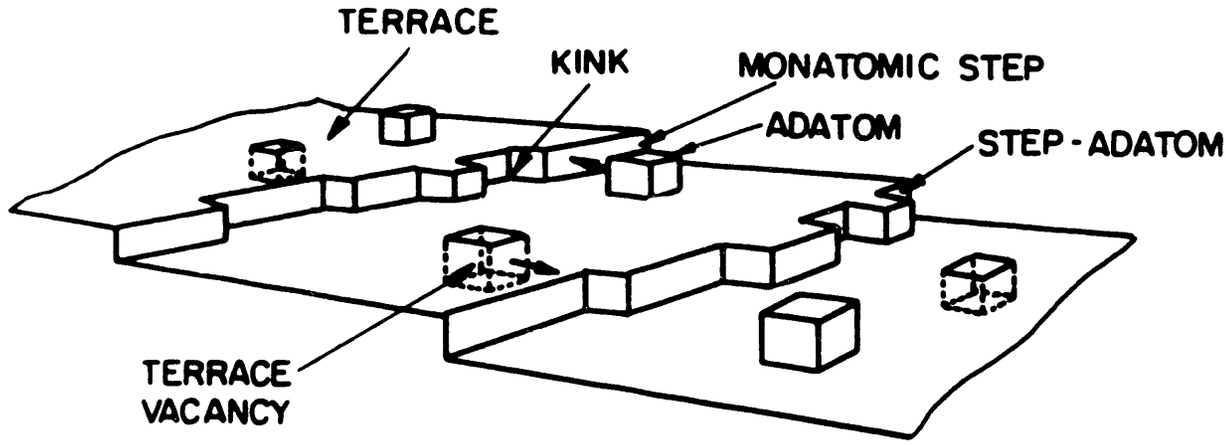

Result:
Friedel oscillation
electronic charge density, n(x)
$n_0$
positive background
exponential decay
-4Å
-2Å
0
2Å
X
XBL 798-6897

Fig. 9




XBL 708-1717A

Fig. 10

# END

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