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CORRELATION BETWEEN CATALYTIC ACTIVITY, BONDING AND COORDINATION NUMBER
OF ATOMS AND MOLECULES ON TRANSITION-METAL SURFACES.
THEORY AND EXPERIMENTAL EVIDENCE.

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Chemistry / Physics

CATALYSIS/TRANSITION METALS/SURFACE STRUCTURE/ELECTRONIC STRUCTURE.

ABSTRACT

Correlation between catalytic activity and low energy local electronic fluctuations in transition metals is proposed. A theory and calculations are presented which indicate that maximum electronic fluctuations take place at high coordination metal sites. Either atomically rough surfaces that expose to the reactant molecules atoms with large number of non-magnetic or weakly magnetic neighbors in the first or second layer at the surface, or stepped and kinked surfaces are the most active in carrying out structure sensitive catalytic reactions. The synthesis of ammonia from N_2 and H_2 over iron and rhenium surfaces, H_2/D_2 exchange over stepped platinum crystal surfaces at low pressures, and the hydrogenolysis (C-C bond breaking) of n-hexane at kinked platinum crystal surfaces are presented as experimental evidence in support of the theory.

INTRODUCTION

Metal catalysts are used to carry out a multitude of selective chemical reactions that range from the synthesis of ammonia from nitrogen and hydrogen gases, to hydrogen-deuterium exchange, to selective hydrocarbon conversion reactions (dehydrocyclization, isomerization, dehydrogenation, and hydrogenolysis to mention a few). These catalysts perform selective bond breaking and rearrangements for millions of turnovers and produce product molecules continuously without deactivation (poisoning). Yet modern surface science studies revealed by isotope labelling and other appropriate experiments that most of the surface is covered with strongly adsorbed species whose turnover is much longer than the times required to produce the desired products for the catalytic reaction [1]. It is therefore obvious that those reaction steps that need metal sites must occur at those few locations on the metal surface that remain uncovered. Thus, the questions arise: How does catalysis occur in the presence of these strongly chemisorbed stagnant layers of almost monolayer coverage? What is the nature of the active metal sites that remain uncovered?

Surface science experiments have also shown that the chemical bonding of adsorbed atoms and molecules is structure sensitive. The heats of adsorption of atoms and molecules could vary as much as 10-30% from adsorption site to adsorption site on the same crystal surface [2]. Top, bridge, three-fold and four-fold sites are available on flat, low Miller index surfaces. Surfaces that are rough on the atomic scale are often

found, by chemisorption or by catalytic reaction studies, to bind atoms and molecules more strongly and to dissociate strong chemical bonds ($\text{N}\equiv\text{N}$, C-H , C-C , C=O) more readily [2]. Rough surfaces are those with higher Miller index where the outermost layer is more sparsely populated, thereby exposing atoms in the second and other inner layers (for example the (111) face of a body-centered cubic crystal as opposed to the (110) face, or the $(11\bar{2}0)$ surface of a hexagonal close packed crystal as opposed to the closed packed (0001) face), or have a high concentration of step edges and kink vertices. The structures of some of these surfaces are shown schematically in Figures 1, 2 and 3.

As a consequence of the structure sensitivity of adsorbate chemical bonding, many of the catalytic reactions are also surface-structure sensitive. The synthesis of ammonia occurs 500 times faster on the more open iron (111) crystal surface than on the close-packed iron (110) crystal face; the reaction on the iron (100) face is in between the other two rates [3]. The same reaction is several thousand times faster on the rhenium $(11\bar{2}0)$ or the rhenium $(10\bar{1}0)$ crystal faces than on the closed-packed rhenium (0001) surface [4]. Hydrogen-deuterium molecular beam studies have revealed that the exchange reaction has almost unity reaction probability upon a single collision with a stepped platinum crystal surface when the beam strikes the open edges [5]. The reaction probability drops by a factor of two when the bottom of the monoatomic-height step is shadowed from the direction of the incoming hydrogen-deuterium mixed beam.

The dehydrocyclization, isomerization and hydrogenolysis reactions of n-hexane and n-heptene on platinum crystal surfaces are all structure sensitive, often varying by factors of 2 to 5 from crystal face to crystal face [6]. Steps often have a beneficial effect, as both C-H and C-C bond breaking seems to accelerate at these defect sites.

One of the key questions in heterogeneous catalysis that emerges from modern surface science studies, concerns the determination of those metal sites where catalytic processes occur; these must be distinctly different from the sites where strong bonding of atoms and molecules takes place accompanied by a low reactivity and slow turnover. In this paper a theory is presented that argues that catalysis is predominant at high-coordination sites: the more bulk-like the site, the greater the probability of electron-state fluctuations which participate catalytically in the breaking and formation of chemical bonds and yield high turnover. This model points out the catalytic importance of metal atoms located in the second layer of open surface structures --the iron (111) surface for example-- which are highly coordinated but are nonetheless exposed to the incoming reactant molecules. Similarly, the increased activity at stepped surfaces is explained by the exposure of high coordination atomic sites at the bottom of the steps.

Adsorbates tend to form strong stable bonds at lower coordination sites, where the atoms have few electron-state fluctuations, where s- and p-bonding predominates, where charge-transfer processes are more common: all these effects lead to the formation of more stable surface compounds.

These low coordination sites have only secondary importance in catalytic reactions that require specific metal sites, as they may sterically block catalytically active high-coordination atomic sites, participate in diffusion or atom transfer processes, or change the local work function.

THEORY

The chemisorption of an atom or molecule B at a given location in an A transition-metal surface is essentially a consequence of the local electronic properties both of the atom or molecule and of the metal site or sites in the immediate neighborhood.

A given electronic configuration of, say, an isolated transition-metal atom A and atom B either leads to the formation of a stable AB compound, or yields an unreactive, no-compound-formation situation. This typical either-or reaction situation is the opposite to what is needed in an effective catalyst, where in principle A should attract B to form a weakly bound AB intermediate compound, but be readily available to release B in the presence of C so that the final product BC be formed and A be ready to start the process all over again.

This traditional view of the intermediate-compound theory of catalysis can be viewed from a different point of view: the particular transition-metal atom A under consideration should be susceptible to stable low-energy electronic fluctuations in its original state. In that case the intermediate AB compound

--intrinsically related to the fluctuations-- can be easily formed. Since low-energy fluctuations are also present after a weak AB is formed, the compound can also be easily broken and the catalytic reaction may thus take place.

The electronic fluctuations of importance may be of many kinds. In particular:

1.- CHARGE FLUCTUATIONS, in which the electronic charge in the vicinity of A fluctuates about its mean value. Atoms of a metal are the traditional examples of charge fluctuators. The classical non-interacting band model of alkali metals, e.g. sodium, has a bulk atom neutral on the average, but with a 1/4 probability each of being positively or negatively singly charged. Electron-electron coulomb repulsion, which is energetically very costly, tends in reality to decrease or suppress large charge fluctuations.

2.- CONFIGURATION FLUCTUATIONS, in which the occupation numbers of single-electron orbitals are no longer good quantum numbers. Transition-metal and rare-earth compounds and structures are typical examples of configuration fluctuators. The nickel configuration alternates, for instance, between $(3d)^{10}$, $(3d)^9 (4s)^1$, and $(3d)^8 (4s)^2$. The cerium atom, a commonly known valence or configuration fluctuator, has its four outer electrons fluctuating among the 4f, 5d, and 6s shells.

3.- SPIN FLUCTUATIONS, in which the magnitude and the orientation of the local magnetic moment fluctuates about its mean vectorial value. Spin fluctuations are common in both metals and insulators, and are very prominent in the rare-earth and in the 3d-transition-metal compounds.

4.- TERM AND MULTIPLET FLUCTUATIONS, present in incomplete shells of complex structure, and common in transition-metal, rare-earth and actinide elemental and compound solids.

All these fluctuations require the presence of low-energy electronic excitations in the spectrum of the structure under consideration. These excitations must have a large spectral weight in the catalytically active site, which in turn must be readily accessible to the reactants and to the release of the final products.

The most important criterion in determining the presence or absence of fluctuations is the location of a given element in the periodic table. There are several tabulations of the heat of adsorption of small molecules (CO , H_2 , O_2 , N_2) on transition metals that exhibit decreasing values with increasing d-shell occupancy [7]. There are also correlations reported for the variations of catalytic activities for hydrogenolysis, hydrogenation, and other chemical reactions that show trends dependent on d-shell occupancy [8,9]. From this evidence it is clear that the catalytic activity of the transition-metal atoms and ions is directly related to their unfilled d-shells. This fact can be rationalized in the following manner.

Both s- and p-shells tend to form deep-lying, filled (bonding) orbitals, highly energetic (several electron volts) unoccupied antibonding orbitals, or wide metallic conduction bands with a relatively low density of states at the Fermi level. None of these situations leads to the

sought-for low-energy fluctuations.

The highly degenerate f-shells are dominated by the very strong electron-electron intra-site coulomb repulsion. As a consequence f-levels, even in metallic structures, are essentially atomic in character: most local charge and configuration fluctuations are suppressed. The levels are essentially discrete and only occasional configuration or term fluctuations, as is the case of cerium, survive.

The d-shells provide the ideal happy medium: the 10-fold degeneracy and relative narrowness of the bands provide metallic character with a high density of states. But the bands are not narrow enough to be dominated by coulomb repulsion effects with the consequent "discretization" of the spectrum, appearance of energy gaps, formation of atomic-like magnetic moments and loss of "metallic" character of the d-orbitals --all conditions which lead to the suppression of local electronic fluctuations.

The effect changes across the periodic table. The electronic fluctuations increase in going from the 3d to the 4d to the 5d series: the d bandwidth increases in that direction, the coulomb repulsion effects are less dominant, magnetism disappears and ordinary configuration fluctuations increase. The effect also increases in going from left to right in the periodic table, with the group VIII elements being the most favorable.

Because of computational considerations we have decided to explore

theoretically in detail the local electronic structure of various surfaces of the late 3d transition metals: Ni, Co, Fe, and Cr. We have also explored heterogenous structures involving either two of these elements, or one of the elements and their noble-metal neighbor, Cu.

The case of nickel is particularly interesting, since it is the last of the 3d, group VIII transition metals. In its metallic form, the ground state is a mixture of three configurations [10] which, on the average, result in the d-shell being occupied by 9.44 electrons. The presence of the $n=0.56$ d-holes, which are a measure of the configuration fluctuations, is responsible for the catalytic activity of Ni. The larger n , the larger the configuration fluctuations of a particular Ni atom, and the greater the catalytic activity of that particular site. Our calculations for nickel in its paramagnetic state --which should also be applicable to palladium and to platinum-- yield a close correlation between n and the coordination number Z of a particular site [10]. Our results are (see Figure 1):

Bulk nickel	$Z(\text{Ni})=12$		$n= 0.56$
(111) Surface nickel atom	$Z(\text{Ni})= 9$		$n= 0.38$
Outstep nickel atom a (Fig. 1)	$Z(\text{Ni})= 7$		$n= 0.25$
Outstep nickel atom b (Fig. 1)	$Z(\text{Ni})= 7$		$n= 0.24$
Instep nickel atom c (Fig. 1)	$Z(\text{Ni})=11$		$n= 0.52$
Instep nickel atom d (Fig. 1)	$Z(\text{Ni})=10$		$n= 0.45$
Ni under a (111) Cu monolayer	$Z(\text{Ni})= 9$	$Z(\text{Cu})= 3$	$n= 0.52$
Ni monolayer on Cu (111)	$Z(\text{Ni})= 3$	$Z(\text{Cu})= 6$	$n= 0.46$

In the list above $Z(A)$ denotes the number of nearest neighbors of chemical species A.

An analysis of the above results yields the following simple conclusion: configuration fluctuations are larger for those atoms which have a large number of metallic neighbors.

Therefore transition-metal atoms in sites which are bulk-like, have a high metallic coordination, and are accessible to the reactants should be, according to this argument, catalytically active.

Another measure of the fluctuations in transition metals is the local spin imbalance at each site. When the coulomb repulsion between electrons becomes strong enough, the system tends to lessen or minimize its influence by suppressing metallic fluctuations. This suppression results in either a tendency towards an insulating state or to the formation of magnetic states [11,12] with local spin imbalance (local magnetic moment) and, at low temperatures, long-range magnetic order (ferromagnetic, antiferromagnetic, ferrimagnetic, spiral arrangements, etc.). As a consequence those conditions which lead to the formation or enhancement of spin imbalances do not favor --i.e. suppress or decrease-- catalytic activity.

We have calculated the spin imbalance S (twice the local magnetic moment divided by the g -factor) for a variety of structures, sites, and circumstances [13-19]. Our results are:

Ferromagnetic bulk fcc nickel	Z(Ni)=12		S= 0.56
Nickel in Ni ₃ Cu quenched alloy	Z(Ni)=8	Z(Cu)=4	S= 0.42
Nickel in NiCu quenched alloy	Z(Ni)=4	Z(Cu)=8	S= 0.08
Nickel in NiCu ₃ quenched alloy	Z(Ni)=0	Z(Cu)=12	S= 0
Nickel at the (100) free surface	Z(Ni)=8		S= 0.74
Nickel at the (111) free surface	Z(Ni)=9		S= 0.65
Nickel under a (100) Cu monolayer	Z(Ni)=8	Z(Cu)=4	S= 0.37
Nickel under a (111) Cu monolayer	Z(Ni)=9	Z(Cu)=3	S= 0.38
Nickel monolayer on top of Cu (100)	Z(Ni)=4	Z(Cu)=4	S= 0.48
Nickel monolayer on top of Cu (111)	Z(Ni)=6	Z(Cu)=3	S= 0.08
Ferromagnetic bulk hcp cobalt	Z(Co)=12		S= 1.56
Cobalt in the FeCo ordered alloy	Z(Fe)=8	Z(Co)=0	S= 1.78
Cobalt at the (100) surface of the FeCo alloy	Z(Fe)=4	Z(Co)=0	S= 2.03
Cobalt at the (110) surface of the FeCo alloy	Z(Fe)=6	Z(Co)=0	S= 1.86
Cobalt monolayer on top of Cu (111)	Z(Co)=6	Z(Cu)=3	S= 1.63
Ferromagnetic bulk bcc iron	Z(Fe)=8		S= 2.12
Iron in the FeCo ordered alloy	Z(Fe)=0	Z(Co)=8	S= 2.66
Iron at the (100) free surface	Z(Fe)=4		S= 2.90
Iron at the (110) free surface	Z(Fe)=6		S= 2.55
Iron at the (100) surface of the FeCo alloy	Z(Fe)=0	Z(Co)=4	S= 2.95
Iron at the (110) surface of the FeCo alloy	Z(Fe)=0	Z(Co)=6	S= 2.75
Iron under a (100) Cr monolayer	Z(Fe)=4	Z(Cu)=4	S= 1.95

Antiferromagnetic bulk chromium (incommensurable phase)	Z(Cr)=8	S= 0.59
Antiferromagnetic bulk chromium (commensurable phase)	Z(Cr)=8	S= 0.67
Chromium at the (100) free surface	Z(Cr)=4	S= 3.00
Chromium at the (110) free surface	Z(Cr)=6	S= 2.31
Chromium monolayer on top of Fe (100)	Z(Cr)=0 Z(Fe)=4	S= 3.63
Chromium monolayer on top of Fe (110)	Z(Cr)=4 Z(Fe)=2	S= 2.25

Four conclusions can be drawn from these numbers:

(i) The removal of nearest neighbors of its own kind reduces the bandwidth of a magnetic transition metal atom, increases the importance of the electron-electron interaction and thus increases the spin imbalance.

(ii) The enhancement of the spin imbalance is important only for those atoms that are not already magnetically saturated; that is, it is large for chromium and iron but relatively unimportant for cobalt and nickel.

(iii) The presence of a strongly magnetized atom as a nearest neighbor tends to increase the spin imbalance of weakly magnetic but polarizable atoms.

(iv) The presence of nonmagnetic, unpolarizable atoms next to a magnetic transition element tends to decrease or completely quench the spin imbalance of the latter.

Since spin imbalances are one of the manifestations of reduced fluctuations, we expect, for a given element, catalytic activity to be anticorrelated to its spin imbalance. This anticorrelation and our

calculations above point once again to catalytically active sites in locations of high coordination, and preferentially to atoms surrounded by a large number of nonmagnetic or weakly magnetic metallic neighbors.

EXPERIMENTAL EVIDENCE

We present here experimental evidence for the high catalytic activity of atomically rough surfaces, where high coordination sites in the first or second layer at the surface are exposed. We also show how stepped surfaces that expose high coordination sites at the step inner edges and at kinks exhibit high turnover rates for various reactions

A.- Greatly enhanced rates of ammonia synthesis on open crystal faces of iron and rhenium that expose the high-coordination atoms in the first and second layers.

The rate determining step in the synthesis of ammonia NH_3 from N_2 and H_2 is the dissociation of dinitrogen [20]. Chemisorption studies indicate that on the open (111) crystal face, where the high coordination iron atoms in the second layer are exposed to the incoming nitrogen molecules, the dissociation probability of N_2 is much higher than on the close-packed (110) face. Chemical reaction studies on iron single crystal surfaces, shown in Figure 4, revealed that the rate of ammonia formation is 500 times greater on the Fe (111) than the Fe (110) face, while the Fe (100) face exhibits catalytic activity which is intermediate between the other two crystal faces [3].

The closed-packed hexagonal rhenium (0001) face is virtually inactive for the synthesis of ammonia, while the open $(10\bar{1}0)$ and $(11\bar{2}0)$ crystal faces have high reactivities, many orders of magnitude higher than the (0001) face [4]. These active crystal surfaces exhibit an open structure with many high coordination sites exposed to the incoming molecules both in the first and in the second layers at the surface. In Figure 5 we show the relative reaction rates on the different single crystal surfaces along with the surface structure displaying atoms of different nearest-neighbor configurations.

B.- Reactive molecular beam surface scattering studies of H_2/D_2 exchange on stepped platinum single crystal surfaces.

The reaction of hydrogen and deuterium molecules to form HD is one of the simplest reactions that take place readily on transition-metal surfaces even at temperatures as low as 100 K. This reaction was studied using mixed molecular beams of H and D on the (111) and stepped surfaces of platinum [5]. The reaction probability was 0.35 on the stepped surfaces, much higher than the 0.07 value on the (111) surface under identical experimental conditions. The reaction probability also depended markedly on the direction of approach of the reactant molecules to the stepped surface. This is shown in Figure 6. The production of HD was the highest when the reactants struck the open side of the step structure, and decreased by about a factor of two when the inner edge of the step was shadowed. These results indicate that the inner corner atom, which is

also the one with the highest coordination, is the most active for breaking the large binding energy (103 kcal) H-H bond.

C.- Enhanced hydrogenolysis activity at kink sites on platinum crystal surfaces.

Platinum is widely used as a catalyst for the rearrangement of hydrocarbons. It is particularly useful for the conversion of straight chain alkanes to aromatic molecules and branched isomers, to produce gasoline with high octane number. The conversion of n-hexane or n-heptane is often used as a test reaction which probes the selectivity of various platinum crystal surfaces to yield the desired products [21]. The hydrogenolysis of alkanes to produce low molecular weight gases --methane through propane-- by C-C bond breaking is an undesirable but important reaction path. It was found that platinum crystal surfaces that have high concentrations of kink sites are the most active ones in carrying out this unwanted reaction [22,23]. This is shown in Figure 7. Hydrogenolysis can be inhibited by the introduction of a small concentration of sulfur that strongly binds to these sites and blocks the C-C bond breaking process.

THE STRUCTURE SENSITIVITY OF CATALYTIC REACTIONS.

The examples of catalytic reactions described above (ammonia synthesis, H_2/D_2 exchange at low pressures and hydrogenolysis) all indicate pronounced structure sensitivity. This structure sensitivity of catalytic reactions can be detected either through systematic variation of metal

particle size [24,25] or by reaction studies using metal single crystal surfaces of different surface structure [26]. For structure sensitive catalysis processes the concentration of the most active metal sites determines the turnover rates. In these circumstances the availability of atoms with high coordination and correspondingly large electronic fluctuations is of key importance. There are also, however, structure insensitive reactions such as many hydrogenation processes [27,28] where the structure of the metal sites is not as important. Reactions of this type are likely to occur on the strongly adsorbed overlayer [29,30] that essentially insulates the metal from most of the reactants and reaction products and may reduce the metal role to that of atomizing some of the smaller reactant molecules (H_2 or O_2 for instance).

As an example, during ethylene hydrogenation a stable ethylidyne monolayer forms on top of the metal surface, and the hydrogenation occurs via hydrogen transfer through this layer to the ethylene molecules which are weakly adsorbed on top of it. The rates of structure sensitive reactions (e.g. the breaking of the H_2 molecule) are controlled by the surface roughness whereas the structure insensitive processes (e.g. the hydrogenation of ethylene by the atomic hydrogen) are mediated by the tenaciously held overlayer. It is important to realize that most catalytic reactions may require both ingredients: the proper atomic surface structure, and a strongly adsorbed overlayer.

CONCLUSION.

The catalytic activity of structure sensitive processes is directly related to the existence of sites with low-energy electronic fluctuations. These fluctuations are most predominant in transition-metal atoms of high coordination number, which are surrounded by a large number of other metallic nonmagnetic or weakly magnetic atoms.

This proposition immediately points out the suitability, for this purpose, of rough, stepped or kinked surfaces of metals and properly chosen alloys, which make accessible to the reactants atomic sites of high coordination.

It is also important to remark that not all intermediate steps of a catalytic reaction are structure sensitive, and that structure insensitive processes (which in general are not the rate-determining ones) may be in fact mediated by tenaciously held overlayers, which insulate the metal from direct contact with some of the reactants.

Our proposition has obviously profound implications in the manufacturing of catalysts, their chemical composition and morphology, as well as in the understanding of the processes that lead both to their effectiveness and to their demise (poisoning).

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FIGURE CAPTIONS

Figure 1 : Geometry for a stepped (111) surface in the face-centered-cubic structure. Open circles are atoms in the second layer, which is complete. Solid circles are atoms in the first layer, in which every third row is removed to create steps. This arrangement can also describe a stepped (0001) surface of a hexagonal close-packed structure (the difference between the two appears in the third, unseen layer).

Figure 2 : Various stepped surfaces in the close-packed face-centered-cubic lattice.

Figure 3 : Various kinked surfaces in the close-packed face-centered-cubic lattice.

Figure 4 : The surface structure sensitivity of the iron catalyzed ammonia synthesis. The symbols C_n indicate n-coordinated sites.

Figure 5 : The strong surface structure sensitivity of ammonia synthesis on rhenium single crystals. The symbols C_n indicate n-coordinated sites.

Figure 6 : The reaction probability for H_2/D_2 exchange over a platinum single crystal surface as a function of angle of incidence θ of the molecular beam, normalized to the incident D_2 intensity. (a) The platinum

(332) surface with the step edges perpendicular to the incident beam. (b) The platinum (332) surface where the projection of the beam on the surface is parallel to the step edges. (c) The smooth, close-packed platinum (111) surface.

Figure 7 : The reaction rates for the hydrogenolysis of iso-butane on various single crystal surfaces of platinum. The kinked (10,8,7) crystal face is the most active for this reaction.

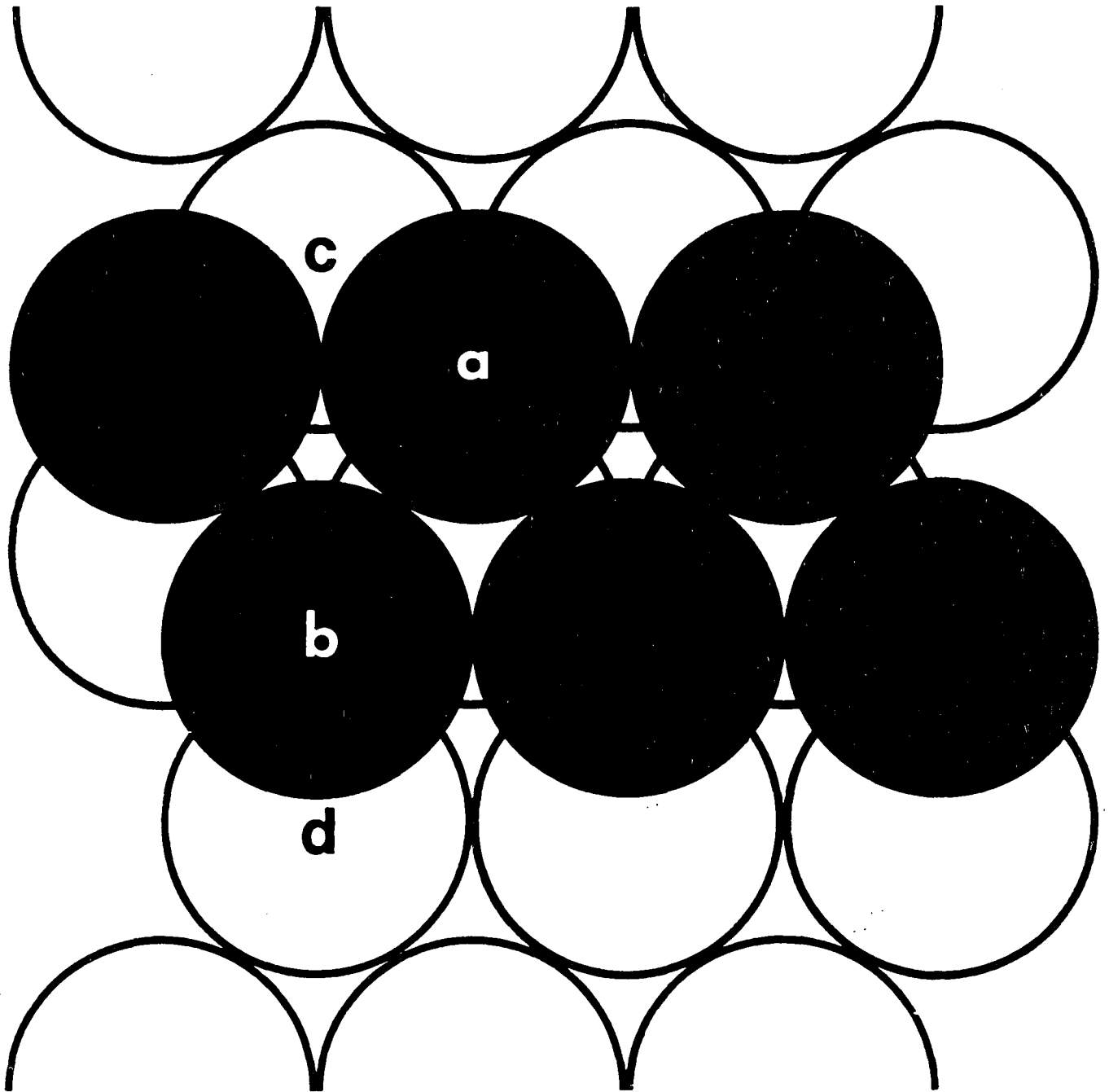
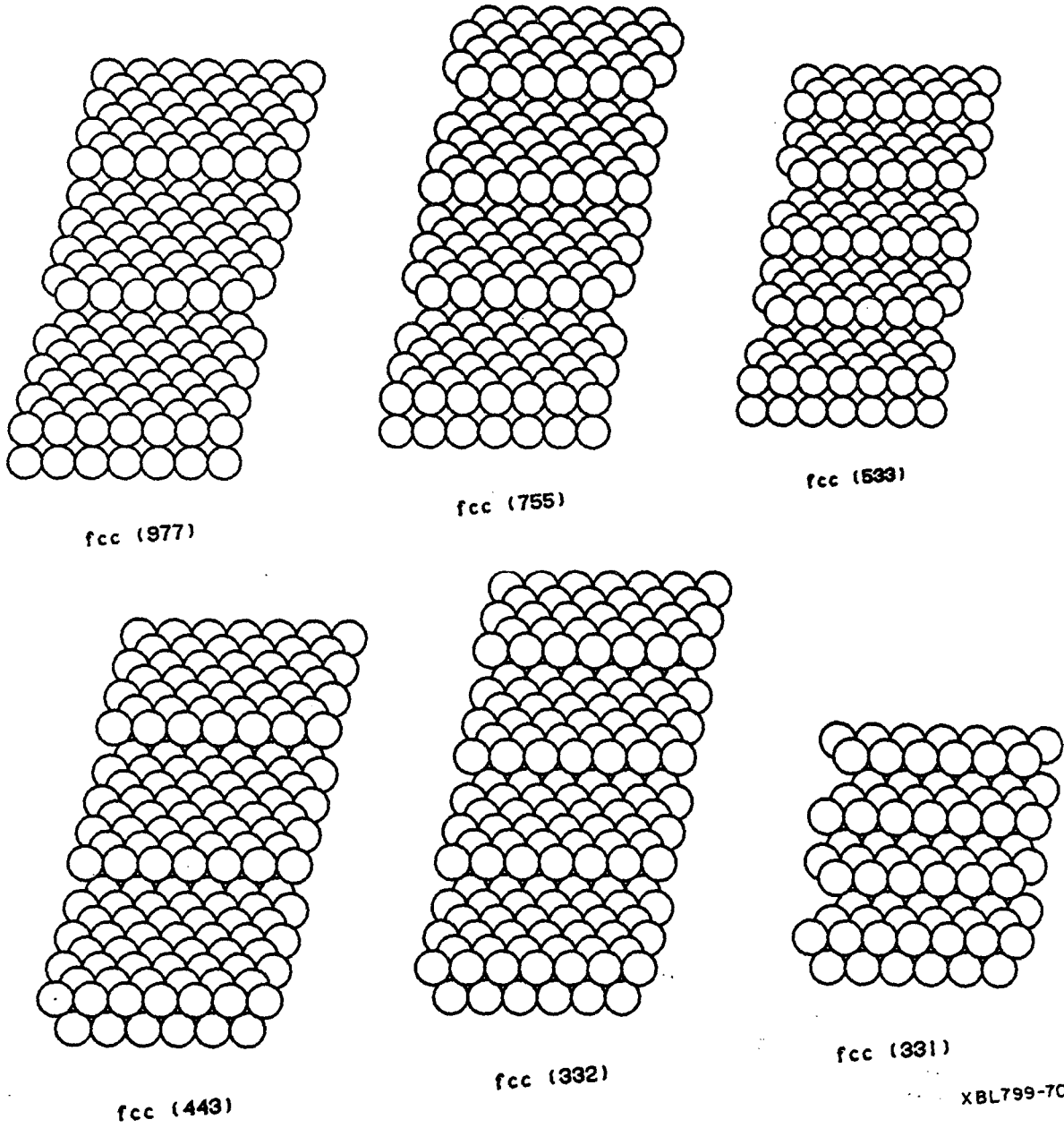
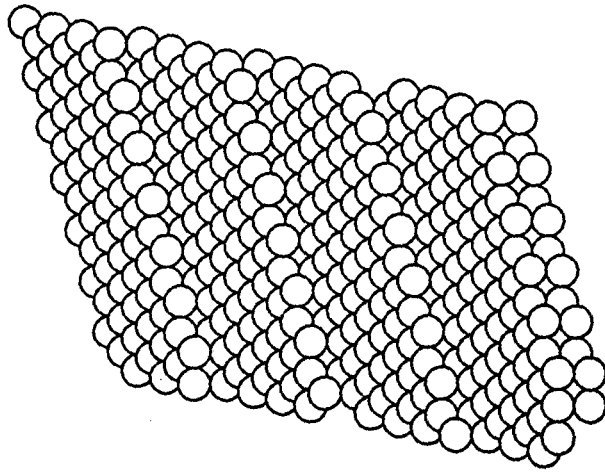


Figure 1



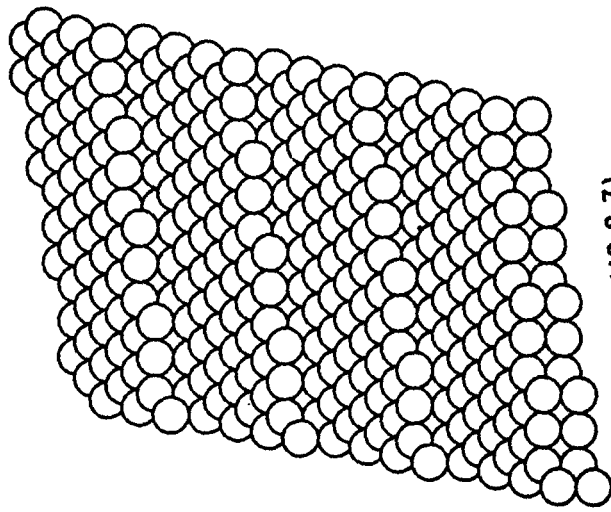
XBL799-7019

Figure 2

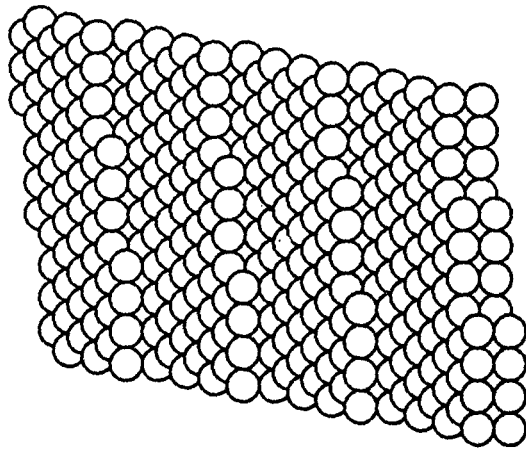


fcc (111, 11, 9)

XBL799-7018

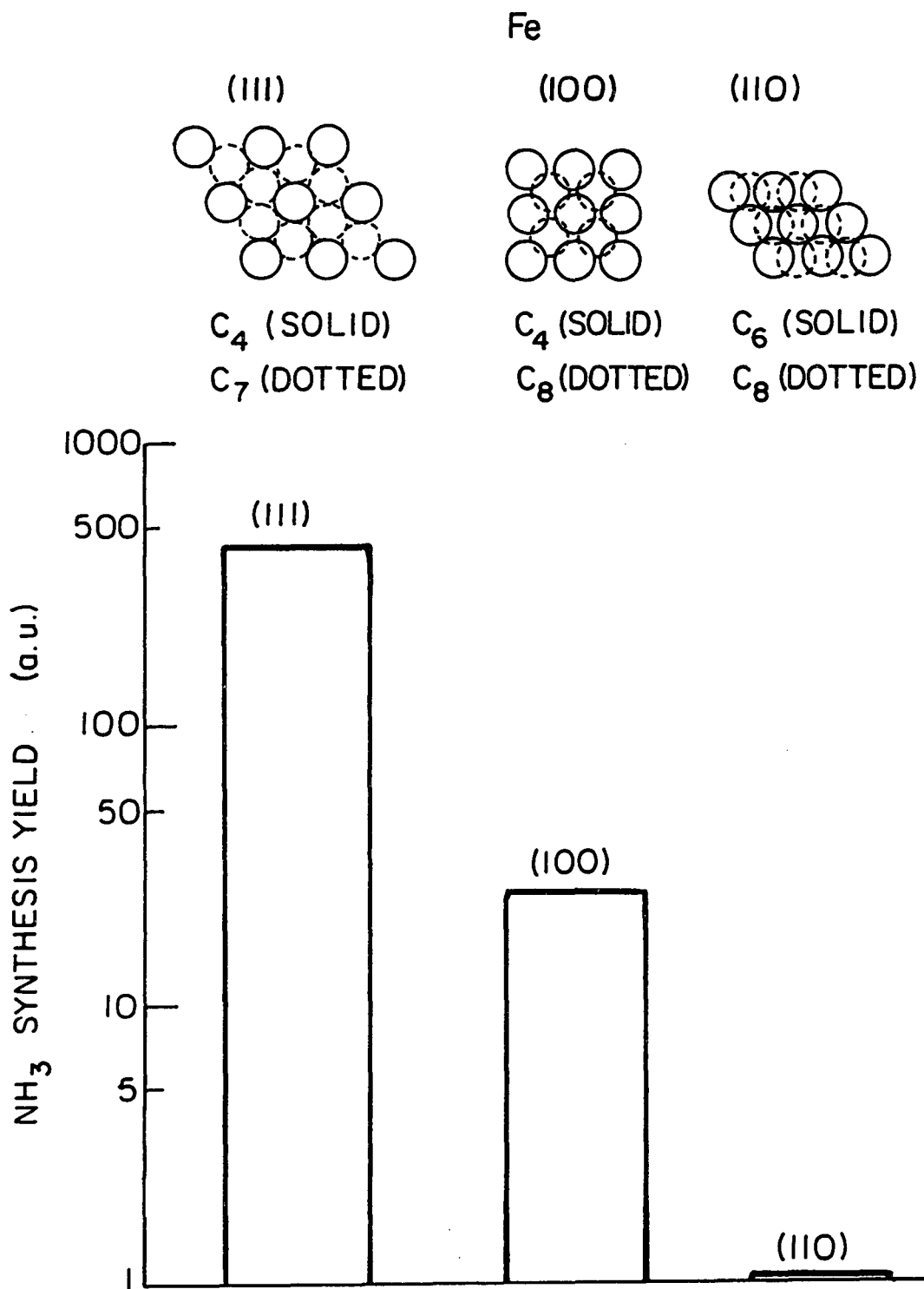


fcc (100, 8, 7)



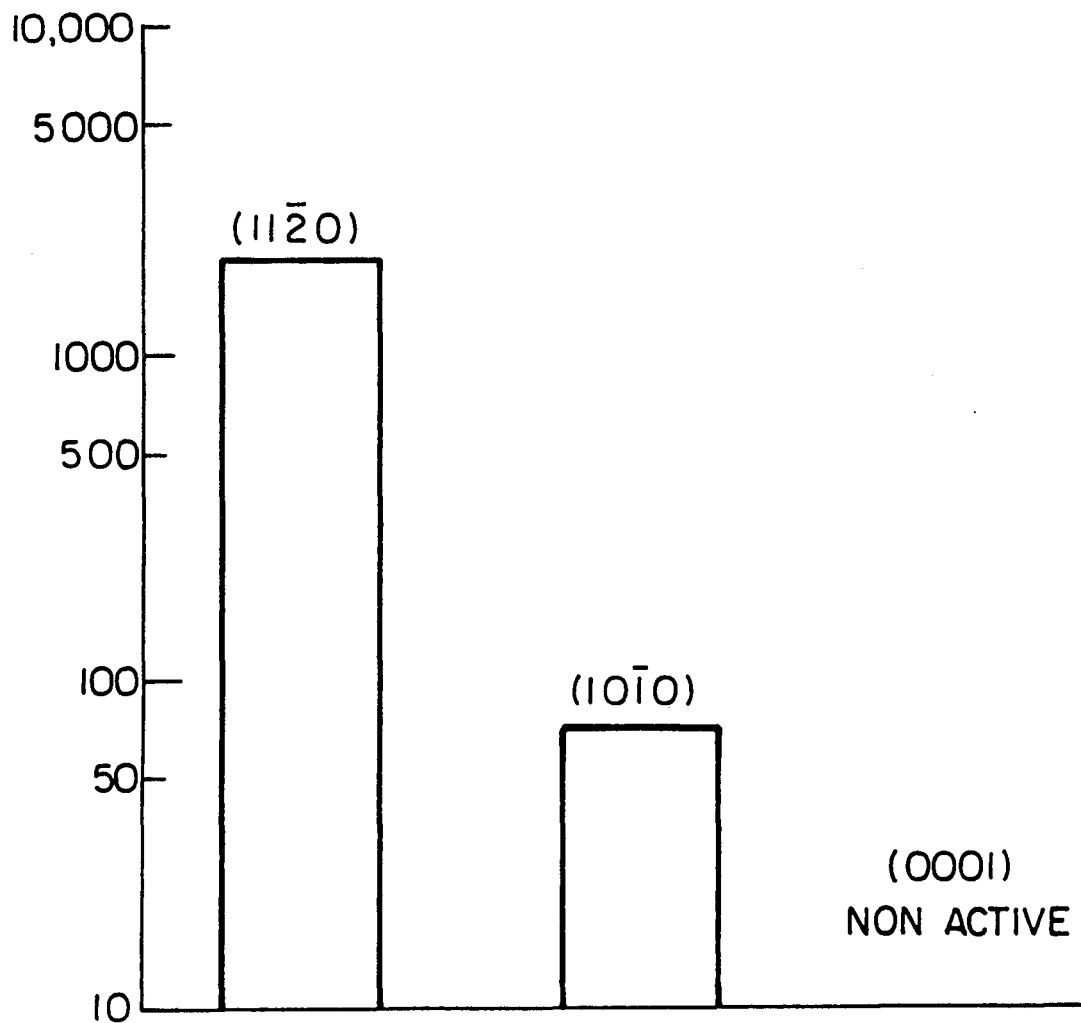
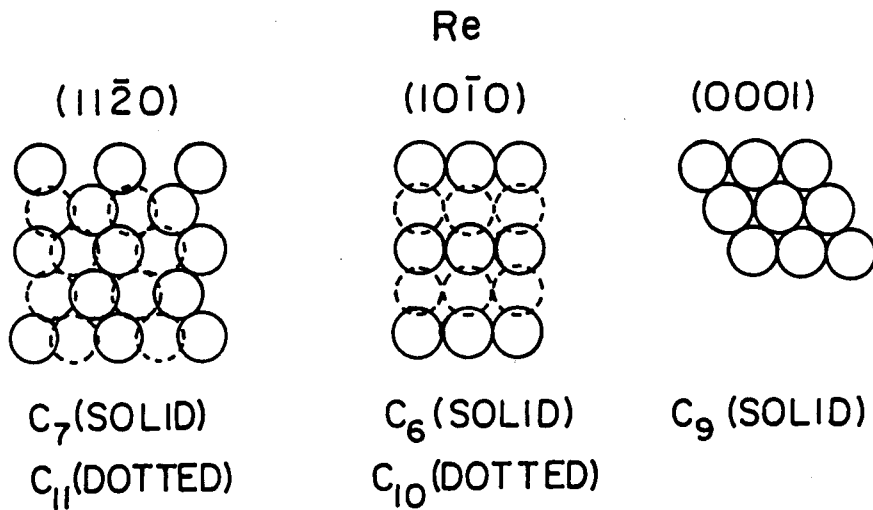
fcc (110, 11, 10)

Figure 3



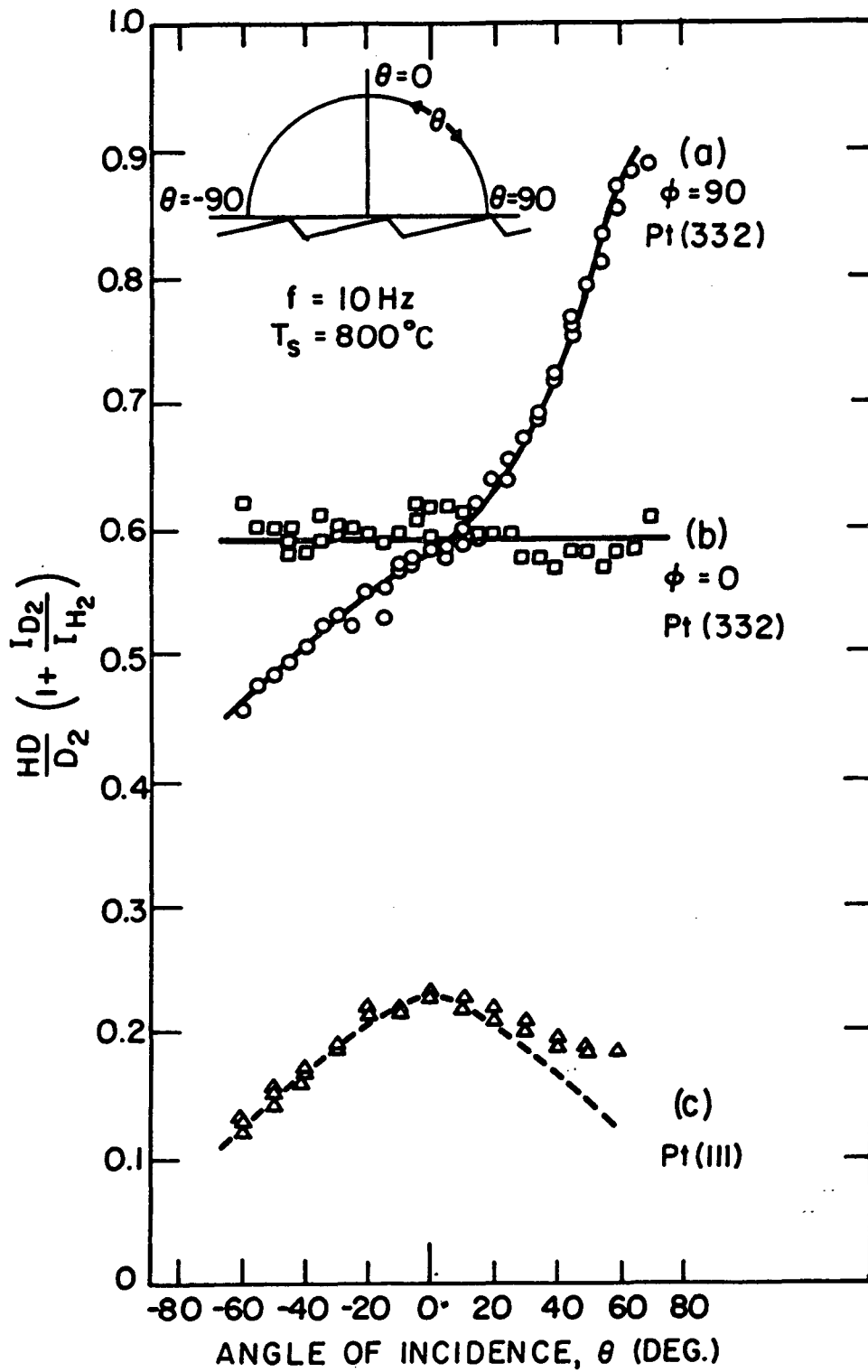
XBL 839-6407

Figure 4



XBL 839-6408

Figure 5



XBL772-5084A

Figure 6

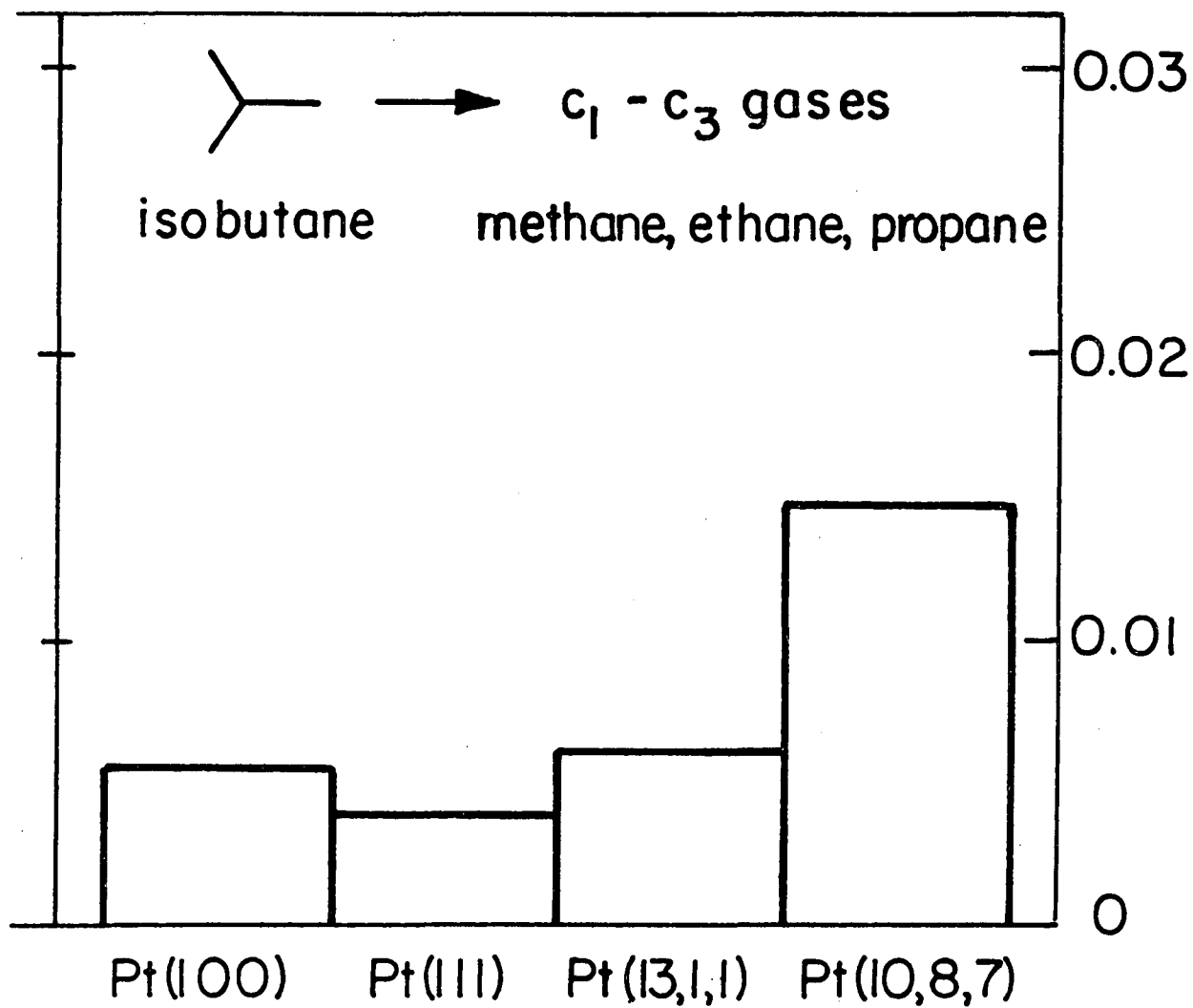


Figure 7

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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