



Title	CATALYSIS AND THE INTERSTITIAL-ELECTRON MODEL FOR METALS : . Characterization of Metal Surfaces
Author(s)	JOHNSON, O.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 20(2), 109-124
Issue Date	1972-08
Doc URL	http://hdl.handle.net/2115/24939
Type	bulletin (article)
File Information	20(2)_P109-124.pdf



[Instructions for use](#)

CATALYSIS AND THE INTERSTITIAL-ELECTRON MODEL FOR METALS

III. Characterization of Metal Surfaces

By

O. JOHNSON*

(Received April 7, 1972)

Abstract

The Interstitial-Electron Model for Metals emphasizes positive metal ion cores (M^{n+}) and itinerant electrons (\bar{e}) localized in interstitial positions in the metal lattice. It is postulated that a greater degree of \bar{e} localization occurs on the metal surface than in the interior but that the surface \bar{e} is also in regions corresponding to interstitial positions. Shifts of \bar{e} on the surface are proposed to adjust for the asymmetry of M^{n+} attraction and \bar{e} repulsion on the surface. The model emphasizes \bar{e} density rather than density of M^{n+} but leads to a description of surface \bar{e} similar to the "electronic charge redistribution" of SMOLUCHOWSKI. Relative binding strength for electrons on different crystal planes for BCC and CCP metals are calculated from the number of M^{n+} attracting \bar{e} above the surface, and these relative binding strengths correlate very well with experimental work functions (ϕ) for the different crystal planes of Cu, Ni, W and Mo. The model also accounts for the major trends in ϕ for metals. There is an indirect influence on ϕ of localized d -electrons on M^{n+} . The model is shown to be compatible with quantum-mechanical and molecular-orbital treatments of \bar{e} on the metal surface.

I. Introduction

The absence of a detailed description of the electron distribution at the metal surface has been a severe handicap to the interpretation and understanding of catalysis by metals. Discussions based on geometric factors¹⁾, electronic factors²⁾, covalent binding of adsorbed molecules^{3,4)}, d -character of metal⁴⁾, ligand field of surface atoms⁵⁾ and on unique surface states⁶⁾ all can give only partial explanations of the complex gradations of catalytic behavior. An attempt will be made in this paper to characterize the surface of metals in terms of location of positive ion cores (M^{n+}) and electrons, \bar{e} . The Hellmann-Feynman Theorem⁷⁾ will be used as a basis for location of electron density in binding regions. The Interstitial-Electron

*) Research Institute for Catalysis, Hokkaido University, Sapporo, Japan; Present address, Institute of Physics, University of Uppsala, Uppsala, Sweden.

O. JOHNSON

Model⁸⁾ will be used here as a guide for localization of \bar{e} density and in a subsequent publication in placing of positive or negative adsorbents on the surface. The metal work function (ϕ) is an important indicator of strength of attachment of electrons to the metal surface and will be used to test the validity of the model.

A complete characterization of the metal surface must answer two extremely difficult questions. The first has to do with the controversial data⁹⁾ on lattice spacings of surface layers. The second has to do with the related electron distribution at the metal surface and its probable variation¹⁰⁾ from that in the interior of the metal structure.

There have been reviews of some of the same problems by GEUS¹¹⁾, BOND¹²⁾, CLARK¹³⁾ and THOMAS¹⁴⁾ from different points of view. The present discussion proposes a new model for metals which makes it possible to discuss \bar{e} in metals in terms comparable to the molecular orbital discussion of \bar{e} in molecules. Although electron energy levels are not emphasized these are also a part of the model and comparisons can be made to treatments involving Fermi levels for \bar{e} in metals.

II. Metal Ion Cores at the Metal Surface

The reports of a drastic change in lattice spacing⁹⁾ at the metal surface have been given alternate interpretations¹¹⁾, and the evidence for a change in lattice spacing from metal interior to surface seems to be limited to 2 cases. RHODIN¹⁵⁾ has reviewed this data and concludes that only in Pt and Au is there compelling evidence for a different surface lattice spacing. These changes amount to a decrease in interatomic distance (a) of 5% for Pt and Au. It is of interest that both of these metals have very high work functions (ϕ). RHODIN¹⁵⁾ suggests that Ir may also exhibit a similar decrease in r_0 at the surface. These relatively small changes in r_0 are in keeping with the observation that many catalytic properties of the metal surface correlate well with bulk properties of the metals¹²⁾. This would not be expected if significant ion core shifts occurred at the surface. GEUS¹¹⁾ has also discussed these observations with similar conclusions. The controversial lattice spacings for 110 and 111 nickel are apparently within 2% of spacing in bulk metal. GEUS emphasizes that the observations of definite changes in spacing for Ag, Au, Pd and Pt are above 250°C and that for most experimental observations of metal properties there is no change in lattice distances at the metal surface.

However, a change which has been demonstrated experimentally is the increase in amplitude of lattice vibrations¹⁷⁾ at the surface and for several

Catalysis and the Interstitial-Electron Model for Metals, III

layers into the interior. This amounts to a 20% increase in amplitude for an average metal. This reflects the absence of repulsion on the surface side of the surface ion cores (M^{n+}). The greater displacement of ion cores at the surface will influence properties such as surface diffusion, surface conductivity, and lead to surface changes during adsorption which will be treated in Part IV. It should be mentioned that under conditions of high temperature catalytic reactions there is considerable movement of M^{n+} and has given rise to the term "catalytic etching"¹⁸⁾. However, this complication does not occur for low temperature adsorption of gases.

Part II gave the spatial extension of metal ion cores and compared them to the intermetallic distance, a . The ion core sizes vary from 0.3 a for alkali metals to 0.43 a for transition metals. Thus, the electrons associated with the ion core are relatively more important for d^{10} ions than rare gas ions. The orientation of d -orbitals⁸⁾ in transition metals is interstitial, *i. e.*, toward itinerant electrons in transition metals with values of $a = 2.6 \text{ \AA}$ or less and orientation is toward other ion cores for metals with $a > 2.6 \text{ \AA}$.

III. Electron Distribution at the Metal Surface

In contrast to the conclusion that there is only minimal shifting of M^{n+} at the metal surface it is anticipated that definite shifts in electron distribution will occur at the metal surface. This is expected from the great mobility of electrons and also from the findings for anions in ionic lattices. In ionic lattices it is concluded that there is a definite shift outward of the anions as compared to cations. This has been interpreted¹⁹⁾ as an adaptation of the more polarizable anions to give greater shielding of the + field of the cations. This is very similar to the proposal of SMOLUCHOWSKI¹⁰⁾ of a "spreading" and a "smoothing" effect on electron density at the metal surface which includes an outward extension of electron density. In the model of SMOLUCHOWSKI, the electronic charge "redistribution" is very dependent on the arrangement of the positive ion cores.

There is no direct experimental evidence for such an outward shift in electrons on the metal surface. An electron shift in d -shell electrons for Zn was considered to be the explanation for the sharp drop in activity for the hydrogen electrode reaction²⁰⁾ from Cu to Zn. It was proposed²¹⁾ that there was a greater electron density (greater screening of Zn ion core) perpendicular to the metal surface for Zn.

The interstitial-electron model shows the location²¹⁾ of itinerant electrons above the surface of M^{n+} , but an assumption must be made as to how far \bar{n} density will extend above the surface. This has been estimated by

O. JOHNSON

other authors from several points of view. HEINE²²⁾ has assumed that the potential of ion cores for the interior of the metal can be considered to extend 1/2 layer above the surface layer. TOYA⁶⁾ makes the same assumption in his discussion of hydrogen chemisorption and places the \bar{e} layer at 1.5 Å above the layer of ion cores. The close packed layers have distances of 0.82 a in metal (a=distance of closest approach). In this paper it will be assumed that \bar{e} can extend 0.5 a above the surface (1/2 layer is 0.41 a). This amounts to 1 Å for metals such as Cu, Ni, Co, Fe and 1.6 Å for Ca and Sr. The details concerning estimates of ion core sizes and the extension of itinerant electrons was given in Part II.

There are two kinds of shifts of \bar{e} on the metal surface. First, when the symmetry of the surface changes due to absence of a layer of M^{n+} above, the \bar{e} will tend to assume a symmetrical position in respect to the ion cores in its vicinity, *e.g.* for the 110 plane of CCP an \bar{e} in a tetrahedral position is much closer to two ion cores than to other neighbors (See Sect. IV, 1), and it is postulated that this \bar{e} becomes centered over the line joining two M^{n+} . Second, there are \bar{e} adjustments due to one sided effects of attraction of M^{n+} in the surface layer and of repulsion by \bar{e} in the surface layer (or a short distance below). This is expected to lead to movement away from the surface for low valent metals (where repulsion by \bar{e} may dominate) but to movement toward the surface for high valent metals. Since the interstitial position is already above the surface of ion cores this last type of \bar{e} is part of the "spreading" effect of SMOLUCHOWSKI. The adjustments for symmetry are part of the "smoothing" effect. Further adjustments to the different screening requirements at the surface will be discussed as the model is described for each of the crystal planes of close-packed metal structures.

IV. Electron Density for Different Lattice Planes of HCP, CCP and BCC Metals

IV-1 CCP Metals

The CCP lattice has oct interstices at centers of edges and the center of the unit cell and tet interstices 1/4 the distance along each of unit cell diagonals. Fig. 1 shows the location of these interstitial positions on the surface of the three major lattice planes. Also shown are the interstitial positions above the plane of M^{n+} (and within the postulated 1/2 layer extension of \bar{e}).

The 100 plane has oct interstices on edges of the unit cell in the plane of M^{n+} and tet interstices 1/4 of a layer above the plane and

Catalysis and the Interstitial-Electron Model for Metals, III

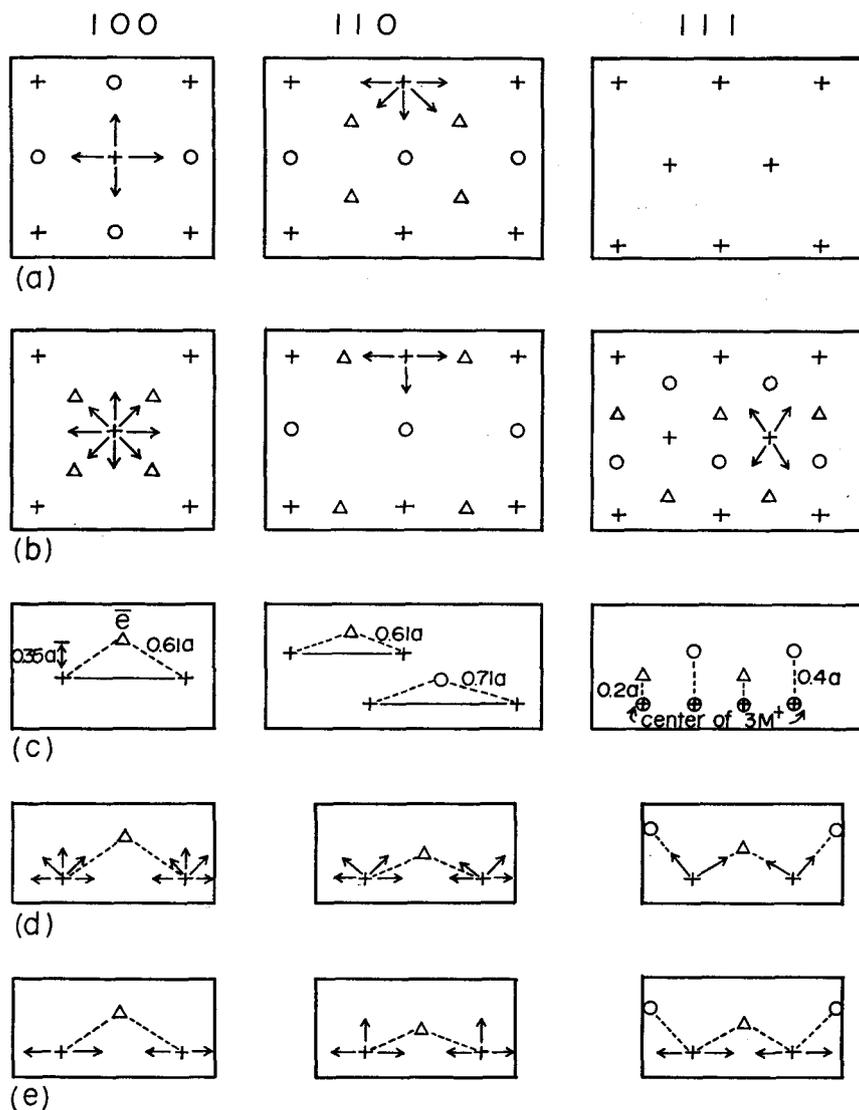


Fig. 1. Itinerant Electrons and d -electrons on and above the Surface of a CCP Metal.

(+ = ion core, O = oct \bar{e} , Δ = tet \bar{e} , \rightarrow = direction of d -orbital)

(a) Ion cores and \bar{e} in surface layer, d -orbitals at 45° to unit cell.

(b) Ion cores in surface with \bar{e} above, d -orbitals shown at 90° .

(c) Cross Section of Surface.

(d and e) Cross sections with d -orbitals shown at 45° and 90° orientation, respectively.

O. JOHNSON

centered above face diagonals. Electrons occupying these tet interstitial positions are 0.35 a above the surface and have 2 M^{n+} as close neighbors at 0.61 a.

The 110 plane has both oct and tet \bar{e} in the plane of ion cores and no interstices above the plane. The oct \bar{e} has 2 M^{n+} neighbors and the tet \bar{e} two M^{n+} as close neighbors. It is postulated that the \bar{e} shifts outward and to a position between 2 M^{n+} for the tet \bar{e} . The minimum distances from 2 M^{n+} would be 0.61 a for tet and 0.71 a for oct.

The 111 plane has no \bar{e} in the plane of ion cores and oct interstices 0.21 a above the plane and tet interstices 0.42 a above, both with 3 M^{n+} as close neighbors to \bar{e} .

A comparison of binding strength of \bar{e} for the 3 lattice planes can be made on the basis of the number of close neighbors (3 M^+/\bar{e} on 111 and 2 M^+/\bar{e} on 100 and 110) and the distance between \bar{e} and M^+ of 0.61 a for 100 and an average of 0.66 a for 110 and 111. Using a $1/r^2$ coulomb force the relative binding strengths are expected to be in the ratio of M^+ neighbors/ r^2 or 3:2.4:2.0 for 111, 100 and 110, respectively. Recent data²³⁾ for work function for different crystal planes of Cu are given in Table 1 and plotted against these gradations of binding strength in Fig. 2, and the correlation with experimentally observed ϕ values is excellent. The data reported by GERLACH AND RHODIN²⁴⁾ for Ni have a large experimental uncertainty, but the data of BAUER *et al.*²⁴⁾ show a deviation for Ni_{100} . ϕ for Ni is influenced by the unsymmetrical nature of *d*-electrons localized on

TABLE 1 Relative binding strength of \bar{e} at metal surface and work function of metal

Rel. Binding Strength			ϕ_{Cu}	ϕ_{Ni}
CCP	110	2.4 (Ni=2.8) ^{a)}	5.155 ± 0.054	5.22
	110	2.0	4.92 ± 0.019	5.04
	111	2.0	5.54 ± 0.012	5.35
			ϕ_{Mo}	ϕ_w
BCC	100	2	4.4	4.60
	110	3	5.1	5.40
	111	(1.8)	4.15	4.40

a) 3.6 for Al and 3.2 for Pb, see text. Work Functions calculated by LANG and KOHN (ref. 25) Aluminum: 100 (4.20 ev.), 111 (4.05), 110 (3.65); Lead: 100 (3.95), 111 (3.85), 110 (3.80).

Catalysis and the Interstitial-Electron Model for Metals, III

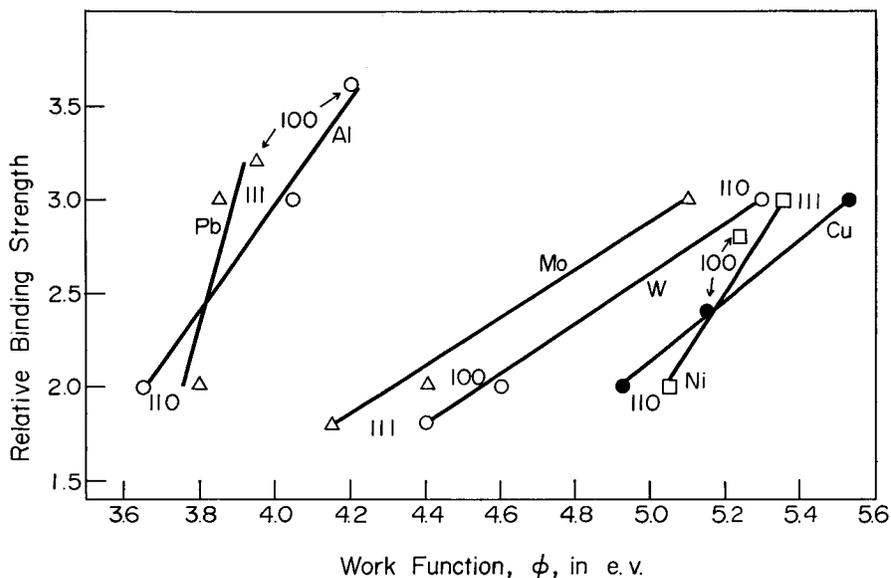


Fig. 2. Dependence of Metal Work Function on Binding Strength of Different Crystal Planes for Electrons.

the ion cores ($\text{Ni}^{10+}(d^8)$) which led to greater tet interstice occupancy and ferromagnetism⁸⁾. The expected changes in ϕ for different lattice planes of Ni are discussed in section V. Recent calculations by LANG AND KOHN²⁵⁾ for CCP lattices predict the above gradation for Cu, Ag and Au.

Metals like Al and Pb have a greater occupancy of tet than oct interstices ($2\bar{e}_{\text{tet}}$, $1\bar{e}_{\text{oct}}$ for Al and $3\bar{e}_{\text{tet}}$, $1\bar{e}_{\text{oct}}$ for Pb)⁸⁾. This means the calculated binding strength must be corrected for the smaller number of electrons above the 100 plane (only tet \bar{e}) ($\times 3/2$ for Al and $\times 4/3$ for Pb). This makes the predicted relative binding strength of surface electrons 3.6, 3 and 2 for Al and 3.2, 3 and 2 for Pb for the 100, 111 and 110 crystal planes, respectively. These agree qualitatively, with the ϕ values calculated by LANG AND KOHN²⁵⁾ using an ion-lattice model for Al and Pb. Repulsive effects of surface electrons have not been directly taken into account in the above estimates, and they become more important for higher valent metals. In principle gradations in ϕ can be predicted for different lattice planes of all metals using the concept of binding strength of electrons. Comparisons of different metals would require evaluation of M^{n+} positive field strengths.

IV-2 BCC Metals

The tet ring interstices⁸⁾ will be considered for \bar{e} above the surface of BCC metals since these offer the greatest number of locations and continuous

O. JOHNSON

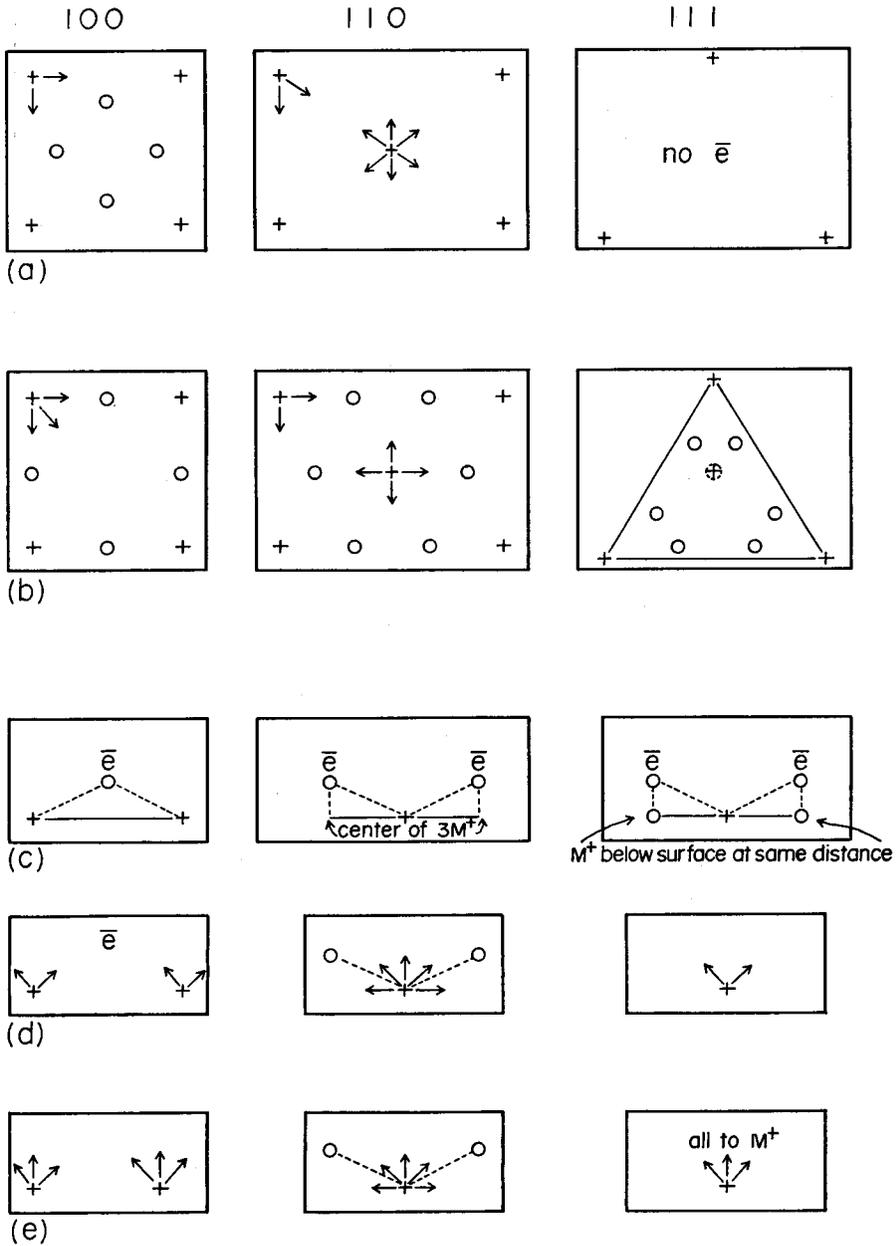


Fig. 3. Itinerant Electrons and *d*-electrons on and above the Metal Surface of a BCC Metal. (Same notations as in Fig. 1)

Catalysis and the Interstitial-Electron Model for Metals, III

pathways to \bar{e} below the metal surface. For the 100 plane there is a tet ring in the surface (Fig. 3) and a tet interstice $1/4$ of an edge distance ($0.29 a$) above the middle of each edge of the unit cell. The distance between layers is $0.58 a$. There are $2 M^+/\text{tet } \bar{e}$. The 110 plane which is the most densely packed plane has no \bar{e} in the surface layer of M^{n+} and has \bar{e} $0.21 a$ above the surface layer with 2 such sites between $+ion$ cores. Each such tet \bar{e} has 3 M^{n+} close neighbors. The 111 plane has \bar{e} at $0.2 a$ above the plane in positions shown in Fig. 3. The 111 plane is the least dense plane and in addition to the 3 M^{n+} shown in Fig. 3 a there are M^{n+} at the centers of the triangle alternately a short distance above and below the plane. Each tet \bar{e} has one M^{n+} neighbor in the plane shown and another M^{n+} at a slightly different perpendicular distance. The $M^+ - \bar{e}$ distances are the same for all BCC crystal planes.

The relative binding strengths for BCC electrons are expected to be 3 for 110, 2 for 100 and ~ 1.8 for 111. This latter is based on an arbitrary correction of 10% for the asymmetry of the 2 M^{n+} . These gradations in binding strength are given in Table 1 and plotted against experimental work functions for Mo and W in Fig. 2. These binding strengths correlate well with the observed work functions of W and Mo²⁶): W; ϕ_{110} (5.3 ± 0.02 ev.) $> \phi_{100}$ (4.58 ± 0.08) $> \phi_{111}$ (4.40 ± 0.03) and Mo; ϕ_{110} (5.10 ± 0.05) $> \phi_{100}$ (4.40 ± 0.05) $> \phi_{111}$ (4.15 ± 0.05). Possible influence of localized d -electrons will be discussed in section V.

IV-3 HCP Metals

For normal HCP lattices the close packed crystal plane (1, 1, 1) will have the same properties as the CCP lattice since there is no distinction due to order of layers at the surface. Possible effects of lattice distortion with $c/a > 1.633$ as for Zn and $c/a < 1.633$ as for Be were discussed²¹ in Part I.

The \bar{e} positions for a crystal plane along the edge of a unit cell and for a plane through the unit cell, both parallel to the c -axis (HCP), are given in Fig. 4. The number of M^{n+}/\bar{e} is 3 in one case and 2 in the others. This leads to a prediction that the 111 plane for HCP lattice has the highest ϕ value.

V. Spatial Extension of Localized d -electrons at the Metal Surface

The interstitial-electron model gives precise information concerning the extension of d -orbitals from surface metal ion cores as well as the occupancy

O. JOHNSON

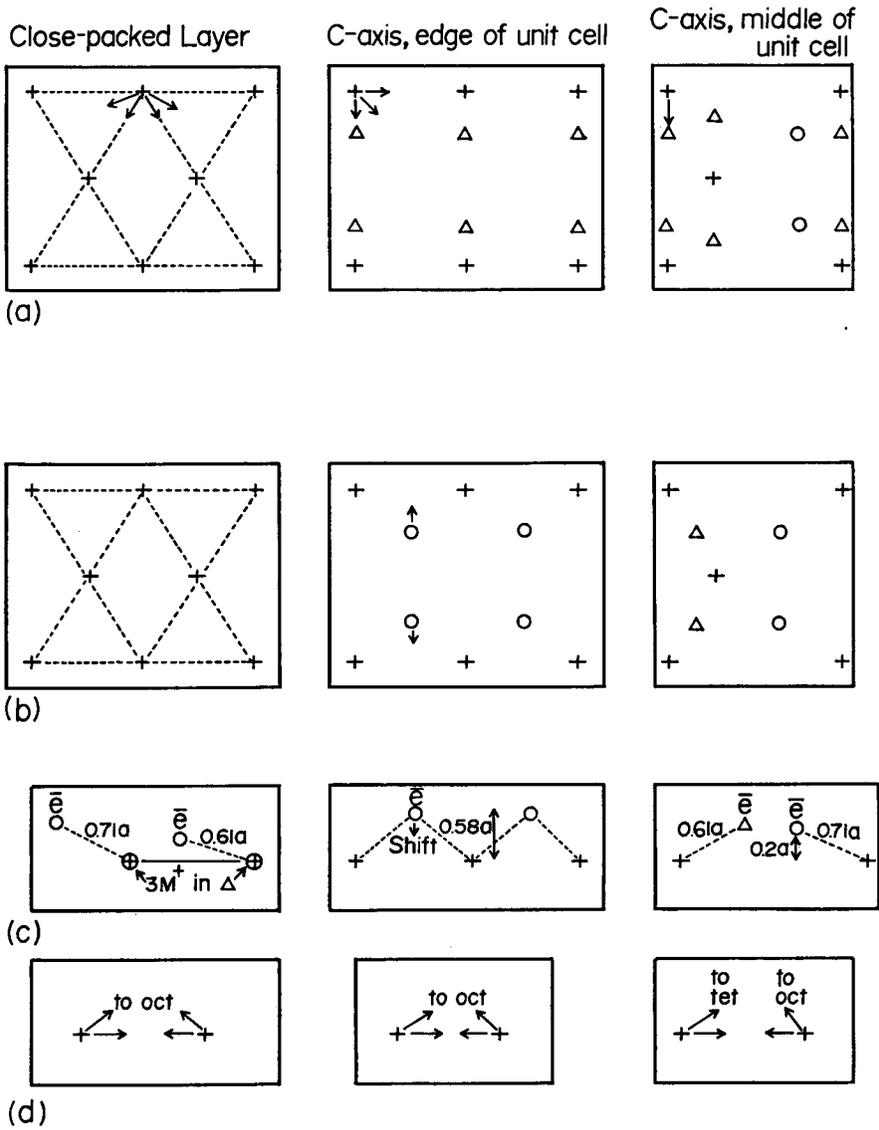


Fig. 4. Itinerant Electrons and *d*-electrons on and above the Surface of an HCP Metal. (Notations the same as in Fig. 1 except only an orientation of *d*-orbitals coincident with a and c axis shown.)

Catalysis and the Interstitial-Electron Model for Metals, III

of these orbitals by unpaired \bar{e} or \bar{e} pairs. These will differ from previously published data of BOND⁵⁾, DOWDEN AND WELLS²⁷⁾ or SHOPOV *et al.*²⁸⁾ because itinerant electrons (treated as ligands) are considered to determine the degeneracy of d -orbitals in the present treatment rather than neighboring M^{n+} .

It is assumed that d -electrons which remain localized to the ion cores do not have as large an energy range as itinerant electrons and that they do not participate directly in determining ϕ values. However, they can indirectly affect ϕ values by repulsive effects on \bar{e} above a metal surface. It is also anticipated that these d -electrons will influence chemisorption in the same way.

To the BCC, CCP and HCP lattices of Fig. 1, 2 and 4 are added d -electron orbitals for the appropriate metals as part of the characterization of a metal surface. The data on ϕ for different lattice planes of Ni offers a chance to estimate the effect of d -electrons.

The major difference for Ni is the occupancy of tet interstices by 1.7 \bar{e} and of oct interstices by 1 \bar{e} , as concluded in the treatment of magnetic properties⁹⁾. Thus, while the interstitial positions for Ni₁₁₀ and Ni₁₁₁ have 2 \bar{e}/M^+ those for Ni₁₀₀ have only 1.7 \bar{e}/M^+ . Correction for the greater electrostatic attraction of this smaller number of electrons changes the estimated binding strength for \bar{e} on Ni₁₀₀ from 2.4 to 2.8. This value is plotted in Fig. 2 and correctly indicated that the ϕ value for this plane should be relatively high.

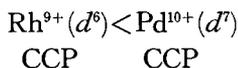
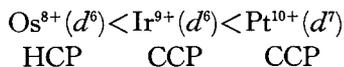
VI. Metal Work Function

The data available on work function²⁶⁾ for different crystal planes has corresponded to the expectations of \bar{e} distribution on the metal surface according to reasonable application of the Interstitial-Electron Model for Metals. It will be of interest to consider in detail the trends in ϕ for different metals since this is considered to be a very important indicator of strength of attachment of \bar{e} to the metal surface. Use will be made of this parameter in discussing chemisorption in Part IV.

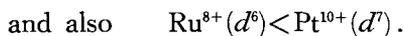
The major trends in work functions are quite clear. For the alkali metals there is a decrease in ϕ from Na to Cs as the effective + field of the ion core decreases with increasing size *i. e.* \bar{e} are not as strongly bound. The increase in ϕ in the order K < Ca < Sc < Ti < V shows the effect of increasing ion core charge in leading to stronger \bar{e} binding. The surprising opposite trends for the d^{10} -metals *e.g.* Cu > Zn > Ga and Au > Hg > Tl were discussed in part I, and it was concluded²¹⁾ that the decisive factor here was the greater core interpenetration by \bar{e} and thus the higher ϕ values.

O. JOHNSON

The transition metals all have work functions greater than 4.3 ev. The high value of ϕ is the result of a strong+ field of ion core which includes localized d -electrons. For transition metals there is an increase in ϕ from the 1st series to the third series. This shows up by an abrupt reversal from $\phi_V > \phi_{Nb} > \phi_{Ta}$ or $\phi_{Ti} > \phi_{Zr} > \phi_{Hf}$ to the opposite gradation in the first metals where the core has d -electrons, *e.g.* $\phi_W > \phi_{Mo} > \phi_{Cr}$ and $\phi_{Os} > \phi_{Ru} > \phi_{Rh}$. The major effect in the transition metals is the presence of d - and f -electrons whose electronic shells screen the nuclear charge to a smaller extent than s and p -electrons. The effect increases from the 1st to 3rd series. This effect also shows up in heats of atomization and interatomic distances²¹. For transition metals even though the ion core charge may be less than that of Ti^{4+} or V^{5+} the lack of screening by d -electrons leads to as strong an attraction for \bar{e} as for the ion cores of greater charge. Within the transition series the following are trends in ϕ showing effects of core charge



There must be specific effects of location of d -orbitals since there are some gradations not expected from either core charges or numbers of d -electrons, *e.g.*



These gradations due to specific effects of d -electrons are not unreasonable in view of the 16% apparent increase in ϕ_{100} of Ni considered to be indirectly due to an asymmetry in d -electrons.

VII. Surface Effects for Small Particles and Thin Films

VII-1 Surface Effects as Shown in Small Crystallites

As the surface decreases to very small dimensions it is usually considered¹⁶ that the collective properties of the metal will no longer prevail, and the chemical binding of the valence electrons will change to a more atomic binding. Previous considerations⁸ of \bar{e} distribution in polyatomic molecules and metal clusters indicate that the valence electrons may still be highly delocalized in smaller units, *e.g.* in metal clusters consisting of 4-6

Catalysis and the Interstitial-Electron Model for Metals, III

metal ion cores. On this basis no drastic change in catalytic properties is expected since metal complexes (related to the metal cluster compounds) have high catalytic activity for many reactions. Much of the data on catalytic activity for small particle size¹⁶⁾ supports this view although this remains a controversial area.

VII-2 Surface Effects as Shown by Properties of Thin Films

Electrical conductivity shows effects of specular reflection resulting from specific interactions of surface ion cores and itinerant electrons since the surface²⁹⁾ roughness (of ion cores) is a major factor here. There is little chance of such measurement leading to information about surface electrons.

Measurement of ferromagnetism of a thin film of Fe on Cu by LIEBERMAN³⁰⁾ has shown for the 1st 2 layers no ferromagnetism develops but a moment of $2.2 \mu_B$ is shown for the 3rd layer. This clearly shows that collective metal properties are not shown until at least a unit cell is present (3 layers for Fe BCC unit cell) since itinerant electrons with a definite arrangement are required to fix the direction of the localized moment on Fe ion cores. It is remarkable that the full ferromagnetism is shown for the minimum number of 3 layers of metal atoms. This observation also suggests that collective metal properties important for catalysis can persist at least down to unit cell discussions *i. e.* 2.92 \AA , cube edge for Fe as a film thickness.

VIII. Comparison of Interstitial-Electron Distribution at Surface with Other Treatments

It appears obvious that treatments of the metal surface in terms of geometry¹⁾, electronic factors such as Fermi Level of metal electrons²⁾, holes in the *d*-band (*d*-character)⁴⁾, or ligand fields and extension of *d*-orbitals⁵⁾ do not deal with the total environment of electrons and ion cores at the metal surface. The quantum mechanical treatments such as those by JANSEN³¹⁾, GRIMLEY³²⁾ and VAN DER AVOIRD³³⁾ are directed more toward the electron distribution in presence of an adsorbed molecule and will be discussed in Part IV in connection with the interpretation of chemisorption by the present model. The quantum mechanical treatment of the metal surface by TOYA⁶⁾ and in particular of hydrogen on metal surfaces by HORIUTI and TOYA⁶⁾ provides a very fundamental basis for electron interactions at the metal surface. The present qualitative model should lead to a very similar picture of $\bar{\epsilon}$ density on the surface if the basic assumptions in the interstitial-electron model for interaction of M^{n+} and $\bar{\epsilon}$ are valid.

O. JOHNSON

The r -states (H adsorbed over M^+) postulated by TOYA for hydrogen adsorption are also indicated in the interstitial-electron model when d -orbitals perpendicular to the surface M^{n+} are vacant. The s -state (H adsorption in interstitial positions) is expected when these orbitals are occupied. Since the r and s -states were developed for H adsorption further discussion will be deferred to Part IV.

Valence bond treatments emphasize interactions of adsorbents with s , p and d -electrons of metal atoms. Although there may be relationships of orbitals of s , p and d -electrons with the interstitial location of \bar{e} in the present model, there is a completely different concept of metal \bar{e} in the interstitial-electron model. The model is best characterized as a M. O. treatment of \bar{e} with provisions for localization of d -electrons on M^{n+} .

IX. Discussion

One of the major conclusions about electrons on the metal surface which emerges from the present treatment is that there is a different localization of \bar{e} density for each lattice plane of a metal. This is the \bar{e} counterpart to the different density of ion cores on each face. This variable \bar{e} density provides a clear distinction between the present model and treatments of the metal surface either purely in terms of band structure or treatments in terms of completely localized binding³¹). This latter difference was aptly termed by ZEMEL³⁴) as the "worms" point of view and "birds" point of view of metals, respectively.

All of the characteristics of interstitial electrons and ion cores developed for the metal lattice as a whole apply to the surface when appropriate modifications are made for local differences in symmetry of M^{n+} . A new feature of the interstitial electron model is that there may be a greater localization of electrons on the surface than in the interior of a metal. This comes about by the change in screening requirements at the surface, *i.e.* there is no longer a layer of M^{n+} above the the surface for which interstitial \bar{e} normally provide screening of $M^{n+}-M^{n+}$ repulsions. From this point of view \bar{e} density is concentrated in interstitial positions. This also is the conclusion from consideration of potentials of M^{n+} along the surface as well as from the point of view of binding regions⁸). Surface \bar{e} contribute to binding of M^{n+} , and the binding regions are the interstitial regions, whereas a small region above M^{n+} is an antibinding region (the special cases where symmetry of \bar{e} was involved led to the opposite situation). Thus, the interstitial-electron model differs from the band model in that it proposes a somewhat greater \bar{e} localization on the metal surface than

Catalysis and the Interstitial-Electron Model for Metals, III

in the interior of the metal lattice. On the other hand, it deviates sharply from a model of localized binding (M^{n+} —adsorbate bonds) in proposing localization of \bar{e} in interstitial positions for most lattice planes (and not localization at each M^{n+}).

The viewpoint on the metal surface of the Interstitial-Electron Model can also be reconciled with the "atomic states" as called for on the basis of photo-electric spectra by THORNBER³⁵⁾ and SPICER³⁶⁾ and on the basis of H-adsorption by SACHTLER³⁷⁾. The binding strength of \bar{e} involved in adsorption, although basically determined by the interactions of the whole metal lattice of ion cores, is decisively influenced by the nearest neighboring M^{n+} (Sect. IV) and in addition is influenced by occupied d -orbitals on that ion core.

It should be emphasized that in the present characterization of the metal surface there are a great variety of \bar{e} positions on the metal surface with different binding strengths and that these \bar{e} are further influenced by the extension of d -electrons into interstitial regions from neighboring M^{n+} .

There have been previous discussions of metal surfaces and catalysis in rather similar terms which have assisted in the present formulation. These range from the early discussions by DE BOER¹⁹⁾ to more recent discussions of catalysis and chemical binding by NYHOLM³⁹⁾, discussion of metals by EHRLICH³⁹⁾ and the treatment in his book on adsorption and catalysis by CLARK¹³⁾.

The discussion in this paper has been a qualitative one with Work Function data the major indicator of behavior of surface electrons. The description in terms of M^{n+} and \bar{e} in the framework of interstices of a metal lattice provides a means of including electron correlation and spin correlation of \bar{e} density. The present characterization of metal surface will be used in clarification of many aspects of chemisorption of H_2 , N_2 , CO and O_2 in Part IV of this series.

References

- 1) A. BALANDIN *et al.*, *Catalysis and Chemical Kinetics*, Ch. 1, Acad. Press., N. Y. and Warsaw, 1964.
- 2) G. M. SCHWAB, *Disc. Farad. Soc.*, **8**, 166 (1950); D. A. DOWDEN, N. MCKENZIE and B. M. W. TRAPNELL, *Proc. Roy. Soc.*, **237 A**, 245 (1956).
- 3) D. D. ELEY, *Disc. Farad. Soc.*, **8**, 34 (1950).
- 4) L. PAULING, *Proc. Roy. Soc.*, **A 196**, 343 (1949); M. Boudart, *J. Am. Chem. Soc.* **72**, 1040 (1950).
- 5) G. G. BOND, *Disc. Farad. Soc.*, **41**, 200 (1966).
- 6) T. TOYA, *This Journal.*, **8**, 209 (1961); J. HORIUTI and T. TOYA, Chap. 1 in *Solid*

O. JOHNSON

- State Surface*, Ed. M. GREEN, Marcel Dekker, New York, 1969.
- 7) See T. BERLIN, *J. Chem. Physics*, **19**, 20 (1951) and discussion in Part II.
 - 8) O. JOHNSON, Series of 6 papers, *Bull. Chem. Soc. Japan*, **45**, 1599, 1607, 1972.
 - 9) R. L. PARK and H. E. FARNSWORTH, *Surface Science*, **2**, 527 (1964).
 - 10) R. SMOLUCHOWSKI, *Phys. Rev.*, **60**, 661 (1941).
 - 11) J. W. GEUS, Chap. 5 in *Chemisorption and Reactions of Metallic Films*, Ed. J. R. Anderson, Acad. Press, New York, 1971.
 - 12) G. C. BOND, *Surface Science*, **18**, 11 (1969); *RIC Reviews* **3**, 1 (1970).
 - 13) A. CLARK, *Theory of Adsorption and Catalysis*, Academic Press, New York, 1970.
 - 14) J. N. THOMAS and W. J. THOMAS, *Introduction to the Principles of Heterogeneous Catalysis*, Academic Press, 1967.
 - 15) T. N. RHODIN, P. M. PALMBERG and E. W. PLUMMER, Paper 22 in *Structure and Chemistry of Solid Surfaces*, Ed. G. A. SOMORJAI, J. Wiley and Sons, New York, 1969.
 - 16) P. B. WEISZ, *Annual Reviews of Physical Chemistry*, **21**, 182 (1969).
 - 17) M. RICH, *Physics Letters*, **4**, 153 (1963).
 - 18) M. BOUDART, in *Fundamentals of Gas-Surface Interaction*, Ed. H. SOLTZBERG, J. N. SMITH, Jr. and M. ROGERS, Academic Press, N. Y., 1967, p. 331.
 - 19) J. H. de BOER, *Adv. in Colloid Science*, **3**, 1 (1950).
 - 20) H. KITA, *J. Electrochem. Soc.*, **113**, 1095 (1966).
 - 21) O. JOHNSON, *This Journal*, **19**, 152 (1971); **20**, 95 (1972).
 - 22) V. HEINE, Paper I, ref. 15; F. Forstmann, J. B. Pendry and V. Heine, *Phys. Rev. Letters*, **24**, 1419 (1970).
 - 23) T. A. DELCHAR, *Surface Science*, **27**, 11 (1971).
 - 24) R. L. GERLACH and T. N. RHODIN, Paper 55-1, ref. 15; R. G. Bauer, R. B. Johnson and G. L. C. Moore, *Surface Science*, **24**, 572 (1971).
 - 25) N. O. LANG and W. KOHN, *Phys., Rev.*, **B3**, 1215 (1971).
 - 26) Data given by J. C. RIVIERE, Chap. 4, *Solid State Surface Science*, Ed. M. Green, Marcel-Dekker, N. Y., 1969.
 - 27) D. A. DOWDEN and D. WELLS, Actes du 2^{me} Congress Int. Catalyse, Editions Technic, Paris, 1961.
 - 28) D. SHOPOV, A. ANDREEV and D. PETKOV, *J. Catalysis*, **13**, 123 (1965).
 - 29) J. W. Geus, Chap., 3, ref. 11.
 - 30) L. N. Lieberman, *Phys. Rev. Letters*, **22**, 539 (1969).
 - 31) L. JANSEN, p. 49 in *Molecular Processes on Solid Surfaces*, Ed. E. DRAUGLIS, R. D. GRETZ, R. J. JAFFE, McGraw-Hill Book Co, N. Y. 1969.
 - 32) T. B. GRIMLEY, p. 299, ref. 31.
 - 33) A. VAN der Avoird, *Surface Science*, **18**, 159 (1969).
 - 34) J. M. ZEMEL, p. 628, ref. 31.
 - 35) K. K. THORNER, *Sc. Prog. (oxf.)*, **57**, 149 (1969).
 - 36) W. E. SPICER, *Phys. Rev.* **161**, 524 (1967).
 - 37) W. H. M. SACHTLER and P. Van der PLANK, *Surface Science*, **18**, 62 (1969).
 - 38) R. G. NYHOLM, International Congress in Catalysis, Amsterdam.
 - 39) G. EHRlich, p. in *Structure and Properties of Thin Films*, Ed. C. A. Neugebauer, J. B. NEWKIRK, D. A. VEIMILYEA, J. Wiley and Sons, N. Y. (1959).