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CATALYSIS AND THE INTERSTITIAL-ELECTRON MODEL FOR METALS

II. Dimensions of Metal Ion Cores and Itinerant Electron Density

By

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Abstract

A model for the metal surface is given in terms of dimensions of positive metal ion cores (M^{n+}) and of electron density of itinerant electrons in $\text{e}/\text{\AA}^3$. The spatial extension of ion cores is obtained from minima in electron density as experimentally observed in X-ray diffraction on metal compounds. Rare gas ion cores extend to 0.31 to 0.32 a (a= intermetallic distance) and d^{10} ion cores extend to 0.43 a. Average \bar{e} density of itinerant electrons is obtained from the known total \bar{e} density of a metal in the volume between the cores (M^{n+}). Average itinerant \bar{e} density varies from $0.01 \text{ e}/\text{\AA}^3$ for Cs to $0.41 \text{ e}/\text{\AA}^3$ for Fe. It is concluded that itinerant electrons are the surface electrons predominantly involved in chemisorption.

I. Introduction

Any treatment of chemisorption and catalysis by metal surface requires a detailed description of metal ion cores and electron density at the metal surface. The previous interstitial-electron description of metals¹⁾ was general in nature and will be extended in this paper to provide the necessary details. The interstitial-electron model assumes that a separation can be made of electron-density associated with the positive metal ion cores and that due to itinerant electrons. The band theory of metals also considers the itinerant electron density to be electron density due to all the metal atoms in the lattice but treats the itinerant electrons in terms of combined wave functions of all the metal atoms. Recent calculations²⁾ of the dimensions of ion cores as well as the experimental determination of electron density distribution from X-ray diffraction³⁾ will be considered. After the extension of ion cores and the electron density in interstices of the metal lattice are formulated for

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the bulk metal lattice, the ion cores and electron density of metal surfaces can be accurately specified.

II. Spatial Extension of Ion-Core Electrons in Metals

There have been a number of models of metal structure which make use of ion cores and ion core radii with the assumption that the core is impenetrable to the itinerant electrons. Some of these models have been used to calculate metal properties with good results. A recent model by RAICH and GOOD⁴⁾ indicates ion cores in metals to be approximately 50% larger than the usual radii of ions in crystals. Another model by STOKES⁵⁾ uses a core radius equal to 3/8 of the intermetallic distance. In some calculations on spectra for Li atoms, PARSONS and WEISSKOPF⁶⁾ find an inner core radius about 1/2 the usual ionic radius beyond which a coulomb potential gave good results for calculation of energy of ground and excited states. Calculation using SCF wave functions²⁾ to determine total electronic charge within a certain distance from + nuclei gave larger ion core sizes than usual crystal radii.

The only experimental data available to determine an ion core size are the very accurate electron densities determined by X-ray diffraction by BENSCH, WITTE and WÖLFEL⁷⁾. Their data show the electron density to be spherically symmetric around Al ion cores, and the electron density drops to an average of $0.2 \text{ e}/\text{\AA}^3$ between the ion cores and in a relatively large region of the total volume. These authors have shown that the integrated average electron density of $0.2 \text{ e}/\text{\AA}^3$ corresponds closely to 3 valence electrons. The electron density map shown in Fig. 1 indicates the feasibility of defining an ion core for aluminum. The electron density is also plotted as a function of intermetallic distance in Fig. 1. There is approach to the average density between ion cores at about 0.9 Å. Extrapolation of the electron densities from the region 0.5 to 0.7 Å gives 0.92 Å as the limit of the ion core electron density in the aluminum crystal. The itinerant electron density can now be obtained by difference, and this aspect is discussed in Section III.

Unfortunately, there are no other data available for metals although it is anticipated that all close packed metals should show well-defined ion cores as found for aluminum. However, there is electron density data available from accurate X-ray diffraction experiments for NaCl, LiF, CaF₂, KCl, MgO, NiO, CuCl, CuBr and Si. (See Fig. 2) For the salts there was observed a definite minimum in electron density between cations and anions, and values for radii of positive ion cores and anions could be readily determined.

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For silicon, as expected, a high electron density of $0.6 \text{ e}/\text{\AA}^3$ persisted in the regions between Si atoms. The electron densities for NaCl and KCl were spherically symmetrical and electron density dropped to zero in the regions not occupied by ions. LiF and CaF₂ showed deviations from spherical symmetry, but ion core radii could be easily defined in these cases as well, even though electron density between ions dropped to only $0.17 \text{ e}/\text{\AA}^3$. The same core radius was obtained for Cu in CuCl and CuBr, although the radius for Cl showed considerable decrease from KCl (1.70 Å) to NaCl (1.64) to CuCl (1.25).

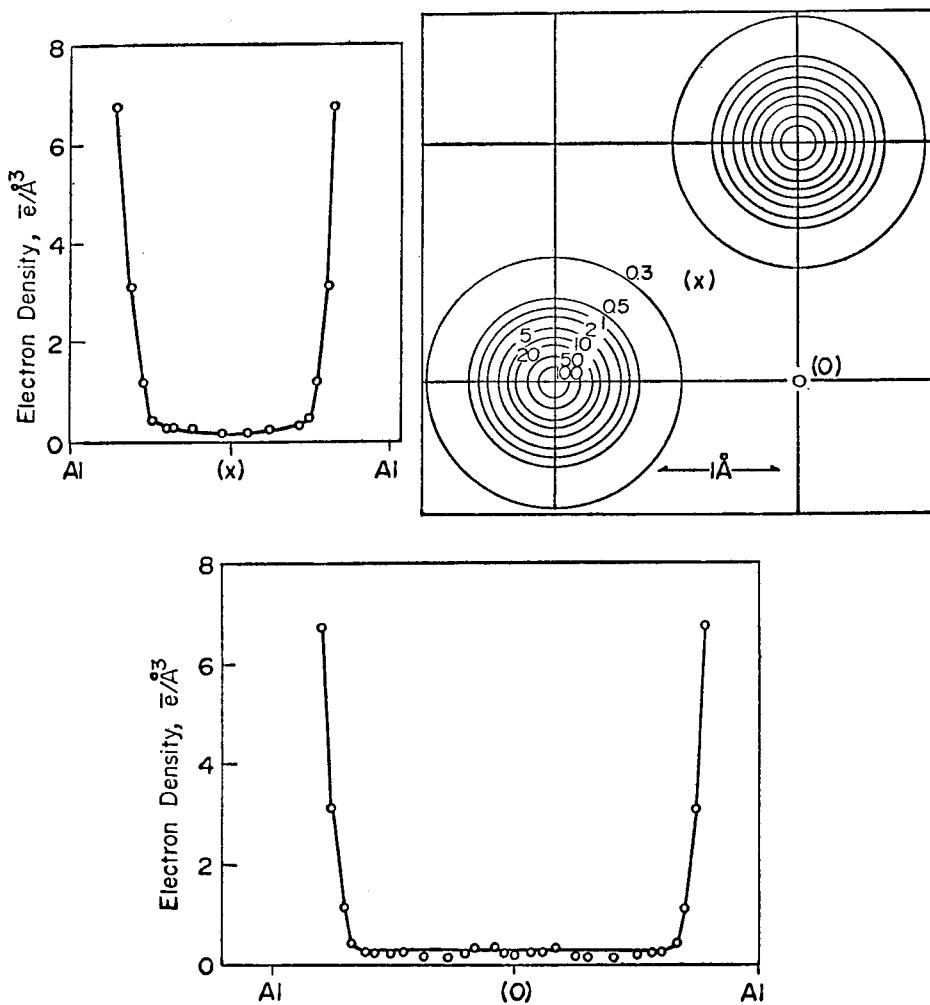
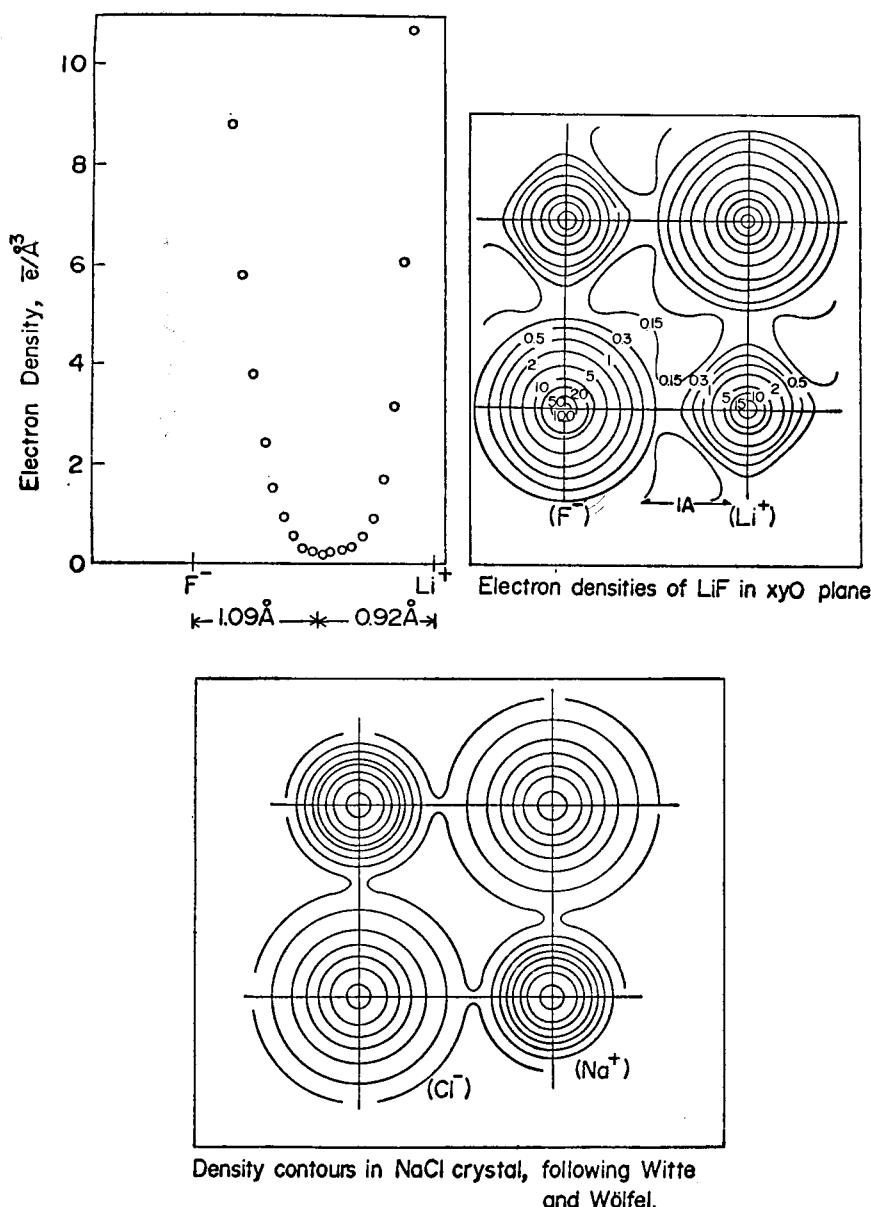


Fig. 1. Electron Density in Aluminum Metal from X-Ray Diffraction.

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**Fig. 2.** Electron Density in NaCl and LiF from X-Ray Diffraction.

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TABLE 1 Relation of positive ion core radius and intermetallic distance

Metal	r_{M^+} , Å	$D_{M/2}$, Å	$r_{M^+}/D_{M/2}$
Li	0.92	1.52	0.61
Na	1.18	1.86	0.635
K	1.45	2.26	0.64
Mg	1.02	1.60	0.64
Ca	1.26	1.97	0.64
Al	0.92	1.43	0.64
Cu	1.10	1.28	0.86
Ni	0.94	1.25	0.75

To test the feasibility of using the positive ion core radii from these X-ray electron density data as the same size as corresponding ion cores in metals, the ratios of r_{M^+} to 1/2 the intermetallic distance ($M/2$) were determined. These are given in Table 1. From these relatively few data it can be concluded that there is a constant ratio of $r_{M^+}/D_{M/2}$ for each of monovalent, divalent and trivalent metals and a different ratio for transition metals and Group IB metals. This relation can be expressed by the equation

$$r_{M^+} = kD_{M/2} \quad (1)$$

where r_{M^+} and $D_{M/2}$ are the ion core radius and 1/2 intermetallic distance, respectively, and k is 0.64 for alkali metals, 0.64 for alkaline earth metals, 0.64 for trivalent metals, 0.86 for Cu and 0.75 for Ni. The two latter are less likely to represent k values for all d^{10} metals or all transition metals, respectively, and remain tentative values. The increase in this ratio for transition metals is reasonable and is due to the decreasing relative intermetallic distance with increasing effective positive core charge (poor screening by d -electrons⁸).

Equation (1) is an empirical relation which can be used to obtain ion core radii for all the metals. It is also possible to establish some theoretical justification for the use of ion core radii derived from ion cores in ionic compounds (*i.e.* positive ion cores surrounded by negative ions) in determining metal ion core radii. This problem can be approached by considering what happens to the electron density of a free ion (M^{n+}) when it is placed in an ionic crystal and into a metal lattice. (See Fig. 3) FAJANS⁹ was probably the first to emphasize that when free ions were placed in a crystal there was tightening or contraction of anions due to the + field of cations and loosening or expansion of polarizable cations, and extensive deformation

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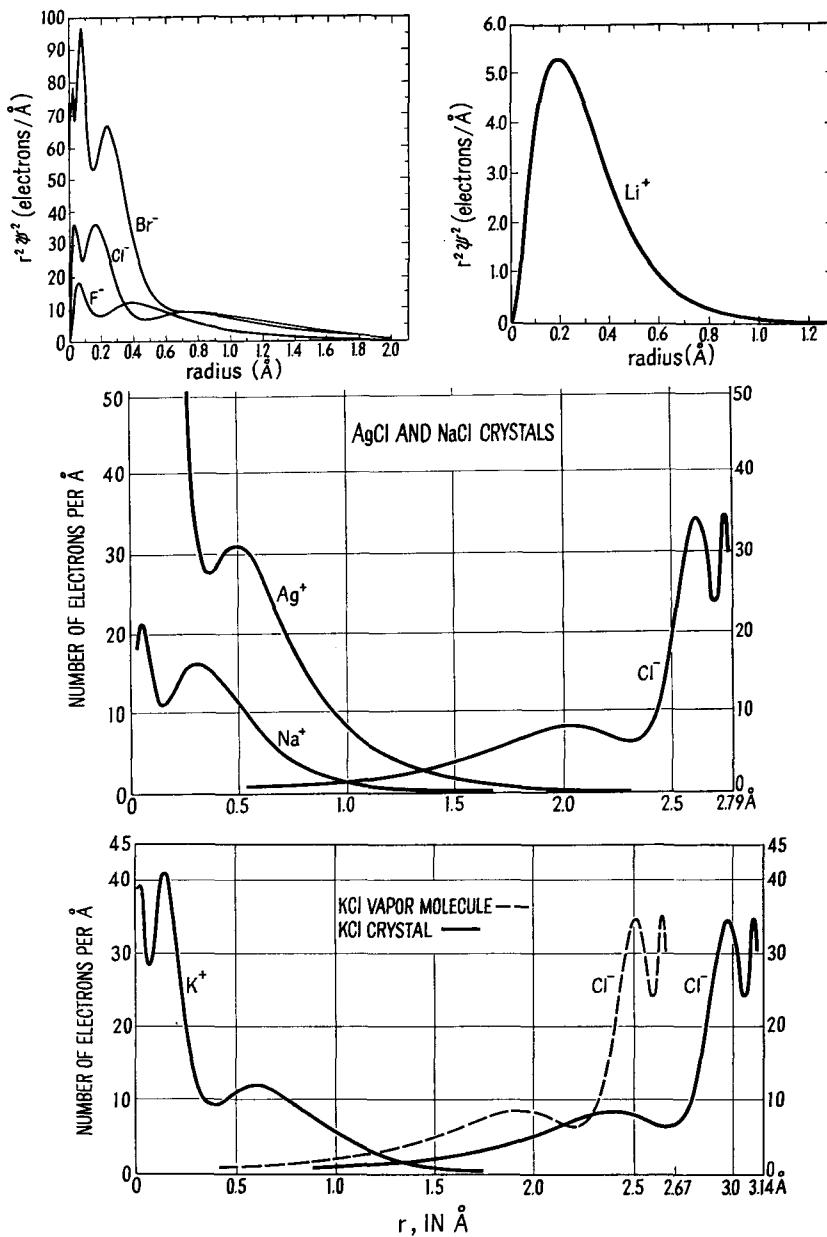


Fig. 3. Radial Electron Density for Li^+ , Na^+ , K^+ , Ag^+ and halides.
(Ions placed at experimental distances in the two lower figures)

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effects in addition, especially for non-rare gas ions. FAJANS also showed the extent of overlap of electron density of free ions such as Na^+ and Cl^- and Ag^+ and Cl^- when placed in a crystal or diatomic molecule¹⁰⁾. In analogous considerations of polarizabilities of ions, FAJANS¹¹⁾ concluded that to correctly represent polarity of alkali halide molecules a correction factor of 0.860 needed to be applied to polarizability of free anions (contraction) and a factor of 1.206 for cations (expansion).

Recently PASCHALIS and WEISS¹²⁾ made calculations using HARTREE-FOCK-ROOTHAAN wave functions for free ions and showed that an expansion of cations and contraction of anions takes place in the potential well represented by surrounding ions. The magnitude of the effect is larger for anions than cations, and in calculations of polarizability changes due to the potential, the results show about a 10-fold greater change for anions. RUFFA¹³⁾ has also shown how the SILVERMAN-OBATA Sum Rule can be used to estimate expansion of free cations in lattices of anions.

Anions will not be treated in this paper; here, the question which needs consideration is whether the spherical field surrounding an ion core in ionic

TABLE 2 Itinerant electron density in metals

Metal	r_{core} , Å	$D_{M/2}$, Å	Core Volume ^{a)} , Å ³	% of Total Volume ^{b)}	Interstitial Volume, Å ³	$\bar{\epsilon}$ density, $\text{e}/\text{Å}^3$
Na	1.18 ^{c)}	1.86	6.9	17.8	31.7	0.03
K	(1.45)	2.26	12.8	17.8	58.9	0.016
Rb	(1.56)	2.44	15.9	17.8	73.1	0.014
Cs	(1.68)	2.62	19.9	17.8	91.5	0.011
Li	0.92	1.52	3.27	15.4	18.7	0.05
Be	(0.7)	1.12	1.44	19.4	6.1	0.33
Mg	1.02	1.60	4.64	19.4	19.5	0.10
Ca	1.26	1.96	8.38	19.4	35.2	0.06
Al	(0.92)	1.43	3.27	19.4	13.7	0.22
Ti	(0.94)	1.47	3.48	19.4	14.6	0.27
V	(0.84)	1.31	2.48	17.8	11.4	0.43
Cu	1.10	1.27	5.6	47.1	6.3	0.16
Zn	(1.07) av.	1.39(av.)	5.13	33.8	10.2	0.20
Ni	0.94	1.25	3.48	31.5	7.8	0.35
Fe	(0.9)	1.26	3.06	24.0	9.69	0.41

a) $4/3 r^3$ or $4.189 r^3$

b) From $r_{\text{c}}/D_{M/2}$ ratio. Close-packed Spheres occupy 74.2% of Total Volume. Spheres in BCC occupy 68% of Volume.

c) Values for Li, Na, K, Mg, Ca, Cu, Ni from X-ray determination. Values in parenthesis calculated as described in text.

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salts is comparable to the field of itinerant electrons. The model used by PASCHALIS and WEISS¹²⁾ is a spherical potential well around the ion core of opposite sign to the ion core at a distance of r_0 . They assume that the potential at r_0 and shorter distances is constant at n/r_0 (where n =charge) and the potential varies as n/r at distances greater than r_0 . Typical values chosen for r_0 were 1.8 Å for Cl⁻, 1.3 Å for Na⁺ and 1.0 Å for Ca²⁺, reasonably close to values of ion core radii (See Table 2). The spherical field of surrounding anions at these distances is then to be compared to the spherical field of ϵ in metals. Since the r_0 values chosen by PASCHALIS and WEISS are of the same order of magnitude as ion core sizes from X-ray density one can expect a similar expansion of free cations in metals and in crystals. Since the field of itinerant electrons (*i.e.*, 0.03 $\epsilon/\text{\AA}^3$ for Na) is expected to be less than for anions (*e.g.*, less than 0.1 $\epsilon/\text{\AA}^3$ for F⁻ at 1.2 Å from Na⁺ in NaF), the values of ion core radii from crystals would represent minimum values for metals. Similarity of lattice energies of metals and corresponding metal halides is another indication of similarity of fields. It can also be mentioned that interionic distances in salts are approximately the same as metal-interstitial-electron distance¹³⁾ in the corresponding metal, *e.g.* NaCl, $r_0=2.82$, Na⁺ to oct. interstice=2.66; KCl, 3.15 and 3.29; LiF, 2.01 and 2.17. Thus, it appears feasible to define an ion core radius for a cation surrounded by a spherically symmetric field of the same charge and opposite sign at the perimeter of the ion core and to use metals as the physical realization of such a model in order to obtain a set of such ion core radii.

For the purposes of considering properties of metals and the metal surface, ion core radii in presence of itinerant electrons will be calculated from equation (1).

These radii will be 0.64 times $D_{M/2}$ for rare gas ions and 0.86 $D_{M/2}$ for d^{10} ions. Transition metal ions remain less definite since nickel was the only ion studied by X-ray diffraction. Here the results of GOLDBERGS²⁾ SCF calculations can be a guide and radii can be empirically determined from compounds using appropriate values for anion radii.

The ion core radii arrived at this way are given in Table 2. Such radii should be very useful with models like those described above and for consideration of many metal properties. It is proposed to use them in this paper to more carefully evaluate the itinerant electron density in metals. It should be mentioned that within the assumption that ion core dimensions are the same in ionic salts and metals, the values in Table 2 are experimental values and are subject to future checking by experimental determina-

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tion of electron density by X-ray diffraction. Table 2 thus gives ionic radii for cations. These radii and the resulting variable anion radii are discussed elsewhere¹⁴⁾.

III. Itinerant Electron Density in Metals

It was shown for aluminum how the definition of an ion-core radius made it possible to calculate itinerant electron density. The flat maximum of itinerant electron density in interstitial positions provides support for the interstitial-electron model¹¹⁾. Itinerant electron density is calculated from the total number of \bar{e} and the volume outside of the ion core volume. Table 2 gives the value for the calculated average itinerant electron density of $0.22 \text{ e}/\text{\AA}^3$ for Al. This is very close to the experimental value of $0.21 \text{ e}/\text{\AA}$ given by BENSCH, WITTE and WÖLFEL⁷⁾.

Electron density in a number of metals have been calculated through use of ion core radii from experimental X-ray electron densities for Na, K, Ca, Mg, Cu and Ni and from equation (1) for the other metals. The variations in itinerant electron density are large and range from $0.011 \text{ e}/\text{\AA}^3$ for Cs to $0.43 \text{ e}/\text{\AA}^3$ for vanadium. Transition metals represented by Ni and Fe also have a high \bar{e} density ($0.35 \text{ e}/\text{\AA}^3$ for Ni, 0.41 for Fe). Calculations of electron density for Ni made by SIROTA and OLEKHNOVICH¹⁵⁾ gave an itinerant electron density in 111 and 110 directions of $0.5 \text{ e}/\text{\AA}^3$. This compares favorably with the value 0.35 in Table 2. (The value of 0.94 for r_c of Ni in NiO also appears the same in Ni metal¹⁴⁾).

A prominent feature of Table 2 is the relatively large ion core of the d^{10} metals, *e.g.* 1.10 \AA for Cu as compared to $1/2$ its intermetallic distance of 1.28 \AA , as was evident in the high ratio in Table 1. This property along with the high positive field of d^{10} cations, which results from the poor screening of nuclear charge by d -electrons⁸⁾ is the major factor in the differences in metal properties¹¹⁾ of noble metals as compared to metals with rare-gas ion cores.

In the interstitial-electron model the electron densities in Table 2 represent average values of electron density in interstices. On an instantaneous basis only a fraction of octahedral or tetrahedral interstices are considered to be occupied by a single electron (or electron-pair for higher valent metals). In addition there is postulated a small degree of localization in one type of interstice¹¹⁾ depending on the metal.

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IV. Relation of *d*-Electrons Localized on Ion Cores to Itinerant Electrons

The ion core dimensions given in Tables 1 and 2 include the *d*-electrons when they are localized on the ion core. Since *d*-orbitals have important directional properties it becomes important to consider them in relation to itinerant electrons.

In an earlier discussion¹⁾ of location of *d*-orbitals in ferromagnetic metals, it was concluded that because of the greater diffuseness of itinerant electrons than *d*-electrons, the *d*-orbitals would be oriented toward interstitial positions for metals of intermetallic distance of 2.6 Å or less and toward other metal ion cores for intermetallic distances greater than 2.6 Å. In considering metal work functions (ϕ) estimates have been made for the strength of attachment of \bar{e} (Paper III). Since the *d*-electrons are expected to have the same upper energy level as itinerant electrons (Fermi level) it was not necessary for consideration of ϕ to directly consider the localized *d*-electrons. Their repulsive effect on adjacent \bar{e} was considered, however. This equation of energy level for \bar{e} and *d*-electrons was used by both TROST¹⁶⁾ and GOODENOUGH¹⁷⁾ in their treatment of metals, and is substantiated by temperature induced shifts from ferromagnetism to paramagnetism in metals and in the insulator-metal transition.

Thus, within the metal structure it will be assumed that except for the ferromagnetic metals at normal temperature, the *d*-electrons specified as localized on ion cores will be considered as completely separate from itinerant electrons with no exchange between them. There can be interpenetration¹⁸⁾ of the more polarizable *d*¹⁰ ion cores by itinerant electrons, with a marked influence on properties of these metal electrons, but also in these metals the itinerant electrons are considered to have no exchange with the *d*-electrons.

V. Ion Cores and Itinerant Electrons on Metal Surfaces

The interstitial-electron model has given a picture of the lattice of metal ion cores and has specified the extension of \bar{e} density of the ion cores and quantitative values for \bar{e} density of itinerant electrons. The expected changes on the metal surface will be discussed in Paper III, but a general picture of ion cores and itinerant electrons for a close-packed metal surface will be given here. The diagrams for rare gas, transition metal and *d*¹⁰ metals given in Fig. 4 assume a maximum extension of itinerant electrons of about 1/2 a layer above the surface of ion cores.

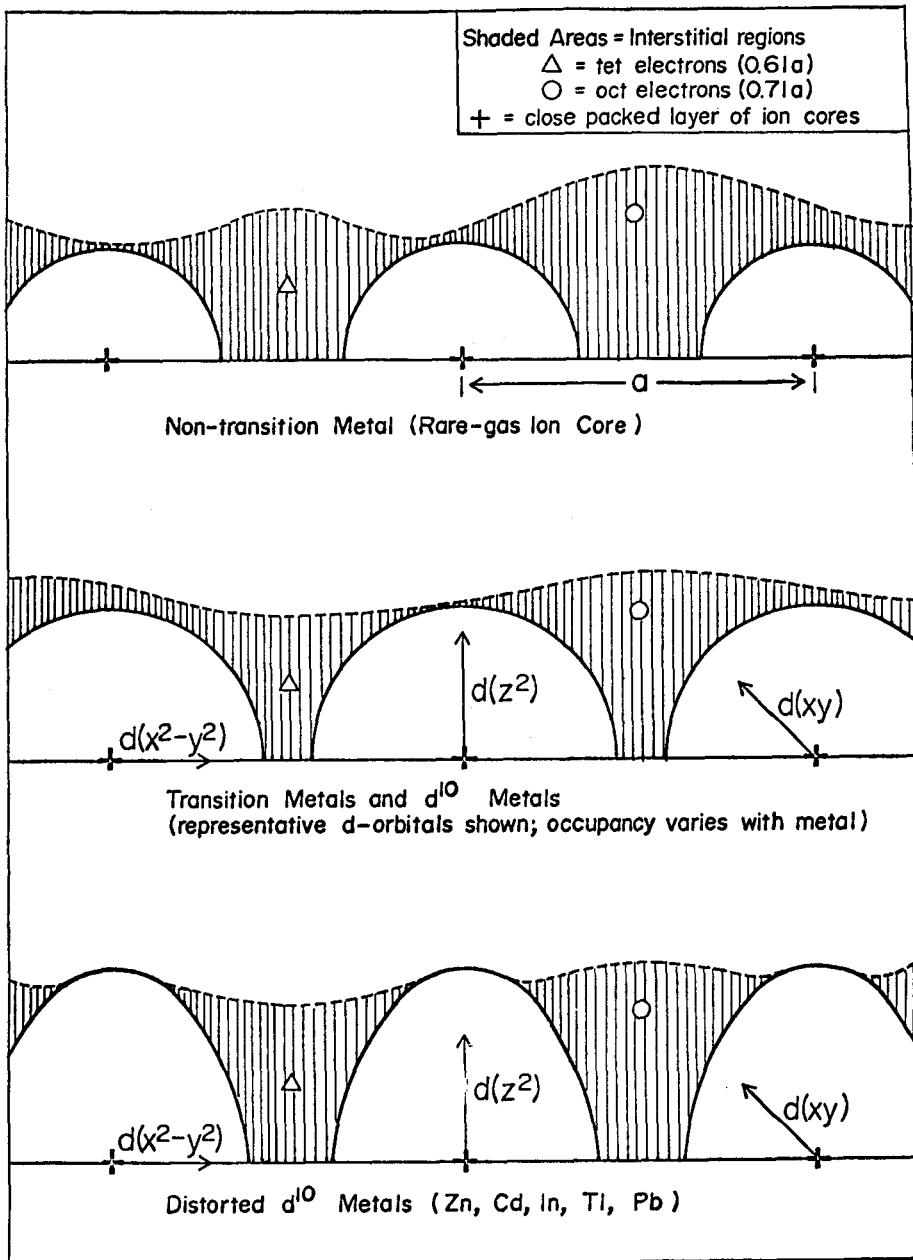
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Fig. 4. Spatial Extension of Ion-Core Electrons and Itinerant Electrons at a Metal Surface (schematic, actual location of interstices between 3 ion cores).

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TABLE 3 Extension of itinerant electrons and ion-core electrons above a metal surface

Metal Ion Core	Maximum in \bar{e} Radial Distribution	Estimated Total Extension of \bar{e} (core)
Rare Gas	0.15 a ¹⁾	0.3 a-0.32 a
d^{10}	0.15 a	0.43 a
Transition Metal	0.15 a-0.18 a (2nd row, 0.22 a, 3rd, 0.25 a)	0.4 a (av.)
Itinerant Electrons	Center of Interstitial Position	Estimated Total Extension of e^2)
CCP, 100 plane	0.35 a (tet)	<u>0.5 a</u>
CCP, 110	0.25 a (oct, tet)	<u>0.4 a (tet)</u> <u>0.5 a (oct)</u>
CCP, 111	0.21 a (tet) 0.42 a (oct)	<u>0.4 a (tet)</u> <u>0.5 a (oct)</u>
BCC, 100	0.29 a	<u>0.5 a</u>
BCC, 110	0.21 a	0.4 a
BCC, 111	0.2 a	0.4 a

1) a = intermetallic distance

2) Values underlined show greater extension of itinerant electrons than d -orbitals in transition metals. The remainder have equivalent extension.

Table 3 summarizes this data and also includes the probable extension of electrons above different lattice planes of BCC and CCP metals. The maxima in radial distribution (HARTREE-FOCH wave functions) are given for comparison.

In anticipation of consideration of chemisorption, a criterion is necessary for deciding whether a given gas is adsorbed by interaction with d -electrons or with itinerant electrons on the surface. It is usually assumed that d -orbitals are involved. However, it appears more likely from the model that itinerant electrons are the most available electrons in many cases. There is experimental substantiation for this in the decrease of $0.6 \mu_B$ per adsorbed H atom¹⁹⁾ in Ni (where the unpaired spin is due to itinerant electrons) and the absence of a magnetic effect for H adsorption on Fe²⁰⁾ (where the moment of $2.2 \mu_B$ is localized on Fe and a decrease would be expected for chemisorption on Fe via d -orbitals).

It will be assumed for the model that in chemisorption on a metal surface the adsorptive will interact at positions of greatest electron density above the surface. This will be at interstitial positions for metals with rare gas ion cores and at both interstitial and d -electron regions for d^{10} and transi-

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tion metals. The non-occupancy of *d*-orbitals perpendicular to the metal surface for many transition metals increases the actual number of metals expected to show preference for interstitial chemisorption. The diagrams in Fig. 4 also make plausible the conclusion reached above that interaction with itinerant electrons will be of major importance except in cases where occupancy of *d*-orbitals affects the screening of the positive field of transition metal ion cores.

VI. Discussion

The above treatment of electrons in metals has led to a precise definition of ion core dimensions and density of itinerant electrons in interstitial regions. This can be compared to the WIGNER-SEITZ treatment of alkali metals²¹⁾, which places \bar{e} in a polyhedron around a metal ion core with boundaries at 0.5 a. It leads to the same electron densities for alkali metals as the model used in this paper.

The interstitial-electron model¹¹ has also assumed that there is some degree of localization of \bar{e} density in interstices (the \bar{e} density values are average \bar{e} densities). This has been done so far in terms of numbers of electrons in octahedral or tetrahedral interstices, but the degree of localization within an interstice has not been specified. The calculations of WANNIER *et. al.*²²⁾ indicating such localization is needed to explain metal cohesion suggest it is of the order of 5%. This degree of localization will be important in treating many metal properties, but for chemisorption and catalysis the localization of \bar{e} density occurring around the chemisorbed atom is undoubtedly much larger than the localization within the metal lattice.

The proposed use of ion core radii for both ionic crystals and metals clarifies the lack of agreement between the X-ray density (experimental) radii of cations and either crystal radii or covalent radii, *e.g.* X-ray density radii for $\text{Na}^+ = 1.18 \text{ \AA}$, crystal radii = 0.97 and covalent or metallic radius = 1.90. The present experimental definition of radii shows the previously used crystal radii to be indefinite quantities actually dependent on the anion present and the metallic radius to include both the ion core and itinerant electrons as represented by (r_{M^+}, \bar{e}) . It is recommended that the experimentally defined ion core radii (SPI) be used along with variable anionic radii (anions can be represented as an ion core surrounded by an electron shell). Intermetallic distances should be used as such and not called metallic, atomic or covalent radii. These new values for ionic radii¹⁴⁾ which have been termed ionic radii for spherical potential ions have been discussed in more detail elsewhere¹⁴⁾.

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