An Interstitial-Electron Model for the Structure of Metals and Alloys I. Description of Model for Metallic Binding

Oliver JOHNSON

Research Institute for Catalysis, Hokkaido University, Sapporo

(Received August 9, 1971)

Application of the Hellmann-Feynman Theorem to Metals has led to an interstitial-electron model in which there is some localization of itinerant electron density in octahedral or tetrahedral interstices of close-packed metal ion cores. A flat maximum of electron density at centers of interstices is proposed as well as preferential occupancy of either octahedral or tetrahedral interstices. Such occupancy is rather precisely determined by the requirements of minimum electron-electron repulsion and of opposite spins for electrons in adjacent interstices. Writing the interstitial-electron structure of a metal in terms of interstice occupancy thus includes electron correlation effects. The interstitial-electron structures are instantaneous pictures of electron density which are representative of the highly dynamic situation of electrons in metals. The model leads to localization of *d*-electrons on the metal-ion core when interstices are fully occupied by itinerant electrons, *i.e.* at M^{6+}. The presence of vacant interstices is required for metallic properties. On the basis of the model, chemical binding in metals differs from that in polyhedral molecules or metal cluster compounds only in the greater delocalization of electron density in metals. The concepts of the interstitial-electron model are closer to those of the method of pseudopotentials than to the Bloch Band Theory although all of these descriptions of metals can be considered equivalent.

The starting point of all discussions of chemical binding must be with electrons and positive nuclei. It is generally accepted that in the metallic state the valence electrons of the metal atom are given up to the whole metal structure as itinerant electrons ($\bar{e}$) which are relatively free to move throughout the lattice of positive ion cores. Intuitively, it seems likely that the maximum binding of such a lattice would be obtained by an optimum distribution of the itinerant electrons within the octahedral and tetrahedral interstices of the metal lattice, *i.e.* some localization of electron density rather than a uniform distribution of electron density. A model with uniform electron density is probably more appropriate for a liquid metal than a solid metal.

In the Band Theory of Metals the wave functions of the itinerant electrons are considered to be extended through the whole lattice and itinerant electrons are described as occupying energy bands. In this paper an interstitial-electron model is presented in which the itinerant electron density is considered to be localized in lattice interstices and presumably, itinerant electron wave functions are not associated with a single atomic core. Since the interstitial-electron model will be developed in terms of spatial location of electrons (*i.e.* electrons-in-interstices) it will not be possible to make direct comparisons to Band Theory which uses energy-momentum coordinates. However, it will be shown that the model can be related to some of the results of the method of pseudopotentials. The view is taken that the interstitial-electron description of metals is equivalent to that of electrons in energy bands, and where energies of electrons are involved, use will be made of Band Theory concepts such as Fermi level and Band width. The model will be presented with a minimum reference to Band Theory of metals since, there have been excellent recent reviews on the topic.[1-3]

1. Background of Interstitial-Electron Model

This paper will give the details of an interstitial-electron model for the structure of metals, and the model will be used in a following series of papers to formulate electronic structure for metals (Part II), to interpret properties of metals (III) including magnetic properties (IV), to explain the formation and structure of intermetallic phases (*e.g.* Cu_5Zn_8) (V) and to give a physical interpretation of superconductivity (VI).

It is difficult to give credit to the large number of investigators who have discussed some aspect of the importance of interstices in metals and related solids. The first proposal of electrons-in-interstices for metals was by Lorentz.[4] Electron pairs at positions of potential minima was proposed for noble metals by Fajans,[5] and Bent[6] has included metals in his tangent-sphere models with electron pairs occupying anionic positions. The model builds as well on important foundations laid by the essentially metallurgical approach of Hume-Rothery[7] and others. The new feature of the present paper is to take the interstitial-model as a definitive description of the metallic state which can incorporate all the quantum chemical aspects of chemical binding including electron correlation and spin. The detailed consideration of the geometry of the HCP and CCP close-packed metals and the BCC metals along with the pattern of interstices in these structures is an integral part of the model.

The Hellmann-Feynman viewpoint[8] offers a means of relating the idea of electron density in interstices to

1) W. M. Lomer, *Prog. Materials Sci.*, **14**, 99 (1969).
2) J. M. Sivertson and M. E. Nicholson, *ibid.*, **9**, 305 (1961). T. B. Massalski and H. W. King, *ibid.*, **10**, 5 (1961).
3) J. M. Ziman, *J. Res. N. Bur. Stand.*, **74A**, 241 (1970).
4) H. A. Lorentz, "Theory of Electrons", Teubner, Leipsig, 1906.
5) K. Fajans, *Ceram. Age*, **54**, 288 (1949); Gordon Conference Lecture, 1959.
6) H. Bent, *J. Chem. Educ.*, **42**, 348 (1965); *Amer. Chem. Soc. Lectures*, 1969—70.
7) W. Hume-Rothery, "The Structure of Metals and Alloys," Institute of Metals, London, (1947).
8) T. Berlin, *J. Chem. Phys.*, **19**, 208 (1951).

general discussions of chemical binding. Berlin and Fajans[9] pointed out clearly that a complete description of chemical binding in a diatomic molecule could be based on considerations of interactions of positively charged atomic cores and electrons. Berlin's[8] analysis of the Hellmann-Feynman Theorem was to point out that at equilibrium the classical coulomb forces exerted by the quantum-mechanical electron distribution on the nuclei must precisely balance the forces of nuclear-nuclear repulsion. The electron density between nuclei in homopolar molecules exerts an attractive force on each nucleus and pulls them together (*i.e.* exerts a binding force). Electron density outside of a critical nodal surface attracts the near nucleus so much more than the far nucleus that there is a net force tending to separate the nuclei, an anti-binding force.

Bader and Jones[10] have applied the Hellmann-Feynman Theorem to many molecules, and this viewpoint has been extended to polyatomic molecules by Bader *et al.*[11] and Bader and Preston.[12] Bader and co-workers have discussed chemical binding by comparing calculated electron densities in molecules with one electron wave functions and resultant electron densities for the constituent atoms. The Berlin analysis of the Hellmann-Feynman Theorem leads to the expectation of a triangular binding region for a triatomic molecule and to a pyramidal binding region for a tetratomic molecule; these are also the conclusions of Bader *et al.* for H_2O and NH_3 based on density difference diagrams.[11,12] Wannier[13] has recently applied the Hellmann-Feynman Theorem to the problem of cohesion in metals. The Hellmann-Feynman viewpoint has been extensively applied to molecules by Bader,[11] Roux and Daudel,[14] Pollisar and Harris,[15] Boyd[16] and Marron,[17] and it appears to be a very fruitful way to discuss chemical binding. The interstitial-electron model proposes a localization of electron density in interstices of a metal structure, and the Hellmann-Feynman Theorem provides a rigorous basis for treatment of forces between electrons and metal ion cores in this binding region.

In extending this viewpoint to metals it is convenient at the same time to define the positive ion core more precisely for a metal. Except for transition metals the ion cores are closed shells of electrons, equivalent to rare gas shells. Berlin[8] has shown that such electrons exert a binding force in molecules since they exert no net force on the nucleus to which they are symmetrical but attract the other nucleus. However, the valence electrons in metals hardly penetrate these ion cores, and the problem of wave functions for itinerant electrons is greatly simplified if it is assumed that the metal positive on cores are not penetrated by valence electrons. This places an additional restriction on the binding region for itinerant electrons in a metal. The binding region in metals is defined by the model as the interstices of the metal lattice, and it is proposed that there are $\bar{e}$ or $\bar{e}_2$ in the octahedral or tetrahedral interstices, *i.e.* electron density centered on the interstice. "Shapes of binding regions" in polyatomic molecules and metals have been discussed more in detail elsewhere.[17a]

Fajans[18] has developed the concept of binding regions in molecules in his Quanticule Theory in terms of quantization of electron or groups of electrons with respect to the positive field of a single nucleus or more than one nuclei. The electronic structure for the tetrahedral molecule B_4Cl_4 is written $[(4B^{3+})\ (\bar{e}_8),\ 4Cl^-]$ where the $(\bar{e}_8)$ group of electrons is termed a quanticule. In the Hellmann-Feynman viewpoint this corresponds to 8 electrons in the tetrahedral binding region which extends out from each triangular face of the tetrahedron. Gillespie[19] has proposed that there are 4 $(\bar{e}_2)$ on the triangular faces of the B_4Cl_4 molecule. When the requirements of electron repulsion and electron spin are imposed on the 8 electrons in the binding region, it seems very reasonable that electrons would be found in the 4 binding regions associated with the triangular faces of the tetrahedral molecule. Delocalization of electrons, as compared to $\bar{e}_2$ between ions, has been proposed by Fajans[18] for benzene and pyrrol and is a widely used concept in Molecular Orbital Theory.

The proposed model for the electronic structure of metals has been discussed thus far in terms of electron density of itinerant electrons in metal interstices. As projected such a model can treat metal properties in a qualitative or semiquantitative way on an electrostatic basis. It is of interest to consider what kind of wave function could represent electron density localized in metal interstice. Non-overlapping wave functions centered on an interstice could be the floating spherical gaussian functions such as used by Frost[20] and also recently by Linnett.[21] The similarity of the present model to Gillespie's[22] treatment of electrons in molecules extends as well to his specification of electron wave functions which are non-overlapping and not centered on atoms. The movement of electrons between such orbitals (or binding regions) will be discussed further in considering the average *vs.* instantaneous electron distribution.

2. Postulates of the Interstitial-Electron Model

The basic postulates of the interstitial-electron model will be given, and this will be followed by a complete

9) K. Fajans and T. Berlin, *J. Chem. Phys.*, **10**, 691 (1942).
10) R. F. W. Bader and G. A. Jones, *Can. J. Chem.*, **39**, 1253 (1961).
11) R. F. W. Bader, *J. Amer. Chem. Soc.*, **86**, 5070 (1964); R. F. W. Bader, I. Keaveny, and G. Runtz, *Can. J. Chem.*, **47**, 2308 (1969).
12) R. F. W. Bader and H. J. T. Preston, *Can. J. Chem.*, **44**, 1131 (1969).
13) G. H. Wannier, C. Misner, and G. Schay, Jr., *Phys. Rev.*, **185**, 983 (1969).
14) M. Roux and R. Daudel, *Compt. Rend.*, **240**, 90 (1955).
15) P. Pollisar and R. R. Harris, *J. Amer. Chem. Soc.*, **92**, 1834 (1970).
16) D. H. Boyd, *J. Chem. Phys.*, **52**, 4846 (1970).
17) M. T. Marron, *ibid.*, **52**, 3600, 3606 (1970).
17a) O. Johnson, Paper Submitted to *J. Chem. Educ.*
18) K. Fajans, "Quanticule theory of Chemical Binding", *Chimia*, **13**, 349 (1959), English Translation available from Ulrich's Book Store, Ann Arbor, Michigan.
19) R. G. Gillespie, Conference on Coordination Chemistry, Banff, British Columbia, (1969).
20) A. A. Frost, *J. Phys. Chem.*, **72**, 1289 (1968).
21) J. W. Linnett, Lecture, U. of California, Berkeley, 1970.
22) R. G. Gillespie, *Angew. Chem. (Int. Edit.)*, **6**, 819 (1967).

description of metal lattices which form the basis of the model. Each of the postulates will be discussed in detail and justifications offered.

I. In a metal the valence electrons belong to the whole structure as itinerant (or conduction) electrons, $\bar{e}$.

$$M \longrightarrow \underset{\text{ion core}}{M^{n+}} + n\bar{e}$$

II. Interstices of the close-packed metal structure are taken as the location of $\bar{e}$. Electron density is centered on an interstice, and there is a flat maximum at the interstice center. It can also be considered that the binding regions for metal electrons are the tetrahedral(tet) and octahedral(oct) interstices.

III. There is preferential $\bar{e}$ occupancy of oct or tet interstices depending on which interstice provides most effective screening from adjacent $\bar{e}$ by positive ion cores.

IV. There are opposite electron spins for $\bar{e}$ in the adjacent interstices with minimum screening. This corresponds to interstices joined by a triangle of metal ion cores.

V. Before the number of $\bar{e}$ reaches 6, the *d*-electrons are localized on the metal ion core, *e.g.* Mn^{7+} (d^5), $2\bar{e}$. The number 6 corresponds to the filling of the 2 tet and 1 oct interstice per M^{n+} with 2 electrons each.

VI. Itinerant electrons in interstices act as ligands and determine the degeneracy of the *d*-electrons localized on the ion core and, thus, their magnetic properties.

VII. For metallic properties there must be some vacant interstices in the metal structure.

VIII. The shape of the oct or tet binding region can change with occupancy since repulsion exerted by electrons in adjacent interstices defines the boundary of the binding region.[17a] Mutual polarization of itinerant electrons and ion cores also modify electron density and "shape of the binding region".

3. Description of the Interstitial-Electron Model

Metal structures have been traditionally discussed in terms of models of close-packed spheres. These are especially useful to show the positions of the tetrahedral(tet) and octahedral(oct) interstices, but it must be emphasized that the observed metal lattice is that of an array of metal ion cores and that the electron density at the periphery of the so-called close-packed spheres is very low. Except for transition metals the metal ion cores are closed shells (rare gas shells).

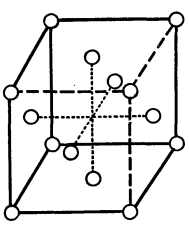
The interstitial-electron model is based on the postulate that in the array of metal ion cores the maximum attraction of these cores by the electrons is obtained when there is some degree of localization of the electron density in the interstices of the structure. A careful consideration of the geometry of each of the close-packed metal structures as well as the pattern of interstices within each structure shows that there are very important differences in interstice distance and arrangement. Each structure will be considered in detail to illustrate the proposed location of electrons according to the interstitial-electron model. The most complete discussion of interstices in crystal lattices has been given by Gehman[23] for Cubic Close Packing (CCP) and for Hexagonal Close Packing (HCP). Gehman emphasized that the occupancy of tetrahedral interstices was the key for understanding the CCP structure of compounds and that octahedral interstices were the key to HCP structures. The present discussion considers electrons in the interstices rather than anions or cations as in Gehman's paper and adds the Body Centered Cubic Structure (BCC). The placement of electrons in interstices offers a natural way to incorporate electron correlation which now becomes inherent in the symmetry of electrons in interstices.

The use of "electron-in-an-interstice" individualizes the electrons in a many-electron system. This is a good approximation[8] and a physically fruitful way to discuss electrons in a metal. This gives an *instantaneous picture* of electron density in oct and tet interstices and includes both occupied and vacant interstices. In the application of the interstitial-electron model it is considered that vacant interstices are required for metallic properties, *e.g.* electrical conductivity. The designation of electron occupancy of interstices (the interstitial-electron structure) is then an instantaneous picture of a highly dynamic situation in which the detailed arrangement is mobile, but the average situation is stationary with high correlation of electronic motion. The model and the interstitial-electron structures to be given are based on short-range correlation of electron position and motion, but the electrons in this arrangement are free to move because of absence of long range correlation of electron repulsions (see *e.g.* Lomer[1]). In the dynamic situation of rapid electron movement and lattice vibrations, the movement of electrons from one orbital to another with many energy states possible is not unlike the models discussed by Hubbard.

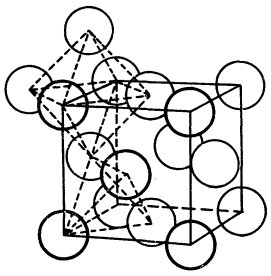
The average itinerant electron density is accurately represented by the instantaneous picture of electrons in interstices, and a time average picture results when the total number of electrons in an interstice type is fractionally distributed over the total number of interstices of that kind. In addition to localization of electron density in one interstice as compared to another (oct more than tet), there can be spatial localization of electron density within one type of interstice (maximum density in center *vs.* more complex distribution). The latter kind of localization may be more important in metal alloys and intermetallic phases and will be discussed in Part V.

Close-packed metal lattices have 2 tetrahedral and 1 octahedral interstice per metal ion core. The interstitial-electron model places electrons in these interstices in the way which gives the maximum screening of positive ion cores by electrons and the minimum electron-electron repulsion. The screening of the electrons from each other by the positive ion cores is very effective, and it is generally assumed[1] that effects of other electrons are screened out within 1 atomic cell. This is also taken to be the case for the interstitial-electron model, and the model can specify which adjacent electrons are least efficiently screened by consideration of geometry of lattices. It will now be

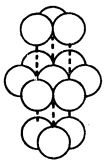
23) W. G. Gehman, *J. Chem. Educ.*, **40**, 54 (1963).



CCP Unit Cell

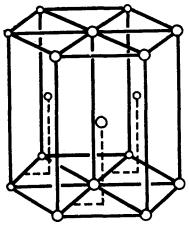


Location of oct and tet interstices
(The CCP unit cell of $4M^{n+}$ has 4 oct interstices per unit cell on centers of each edge and at the center of the unit cell. The 8 tet interstices per unit cell form a cube around each M^{n+}.)

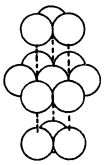


Packing of layers in CCP

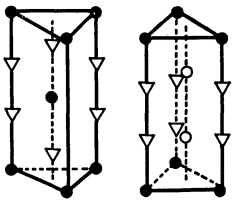
Fig. 1. Structure and location of interstices in CCP metals.



HCP unit cell



Packing of layers in HCP



Location of oct and tet interstices (●=ion core, ○=oct, ▽=tet).
The HCP unit cell of $2M^{n+}$ has 2 oct interstices within the cell. Oct interstices form a trigonal prism around M^{n+}. The 4 tet intersices per unit cell are along the *c*-axis in pairs between all M^{n+}. They form a double set of tetrahedra around M^{n+} (C_{3h} symmetry).

Fig. 2. Structure and location of interstices in hexagonal close packed metals.

shown how the geometry and symmetry of the interstices can lead to definitive assignments of electrons to the interstices in different metal structures.

In the CCP structure shown in Fig. 1 there is a symmetrical arrangement of interconnected octahedral and tetrahedral interstices. The screening between octahedral electrons and tetrahedral electrons is by a triangle of close-packed metal ion cores. Tetrahedral and octahedral electrons are screened from each other by metal ion cores along a tetrahedral edge. Thus, the important distance establishing electron-electron repulsion is that between tetrahedral and octahedral interstices in CCP or 0.61 *a*, where *a* is the distance of closest approach. The maximum screening occurs between tet interstices. This comes about because an oct interstice is joined to 12 other oct interstices by 12 edges and to 6 tet by triangular faces while a tet interstice is joined to 6 adjacent tet interstices by edges and to four oct interstices by triangular faces. It can be concluded that in the absence of other controlling factors CCP metals will show a preference for tetrahedral occupancy of interstices by itinerant electrons. Interstice Distances for CCP, HCP, and BCC structures are given in Table 1.

The HCP structure shown in Fig. 2 has interconnected octahedral interstices in a line perpendicular to the layers. This is a consequence of the above arrangement of close-packed layers. The tetrahedral interstices occur in interconnected pairs which are screened from other pairs by an ion core. Thus, in the HCP metals all interstices are involved in mutual electron-electron repulsions. The distances between them are the following: oct-oct, 0.82 *a*; oct-tet, 0.61 *a*; tet-tet, 0.41 *a*. The latter, very short distance is only applicable when over 1/2 of the tet interstices are occupied. For low $\bar{e}$ occupancy there will be a preference for tet occupancy because with 1 $\bar{e}$ per tet there is screening by ion cores. With 2 $\bar{e}$ in tet there is strong $\bar{e}$-$\bar{e}$ repulsion in tet, and the greater interstice distance for oct-oct makes for a preference for octahedral interstice occupancy in HCP. These conclusions as to interstice preference agree with the conclusions of Gehman based on metal compounds.

The distorted HCP structures require special treatment. When the *c*/*a* ratio is greater than 1.633 *a* as in Zn or Cd there is an increase in oct-oct distance which is greater than the oct-tet increase. The octahedral preference is enhanced. However, when there is less than half occupancy of tet interstices as is the case for Zn, there is a stronger tet preference since these electrons are completely screened from each other by ion cores just as in Normal HCP. The HCP lattices with the opposite distortion, *c*/*a* less than 1.633 *a*, can be considered to have the pair of tet interstices changed to a single bi-pyramidal (bipyr) interstice.[24] This is the structure observed for Be, Sc, Y, and a few other metals. Since the structure now has 1 oct and 1 bipyr interstice per metal ion core, this structure differs greatly from the normal metal with 1 oct and 2 tet interstices per ion core. There are 2 factors influencing occupancy here; the tet interstices are the ones completely screened by an ion core but the oct-oct distance is much greater than oct-tet. Becasue of spin restrictions there appears to be a restriction on oct occupancy in this type of distorted HCP (see discussion below).

The BCC structures are not close-packed, but inter-

TABLE 1. INTERSTICE DISTANCES IN METAL STRUCTURES[a]

Distance	CCP	HCP	BCC
Unit Cell Edge	1.414	1[b]	1.155
tet-tet ($^1/_2$)	1	1	0.82
tet-tet	0.71	0.41	0.41,0.58
oct-oct	1	0.82	0.41,0.58
oct-tet	0.61	0.61	—
M^{n+}-oct	0.71	0.71	0.58,0.81
M^{n+}-tet	0.61	0.61	0.645[c]

a) Distances also given in S. Ho and B. E. Douglas, *J. Chem. Educ.*, **46**, 207 (1969).
b) Distance of closest approach taken as 1.
c) Distance to two nearest tet interstices.

24) A. Kjershus and W. B. Pearson in H. Reiss, Progress in Solid State Chemistry, Vol. I, Pergammon Press, Oxford, 1964.

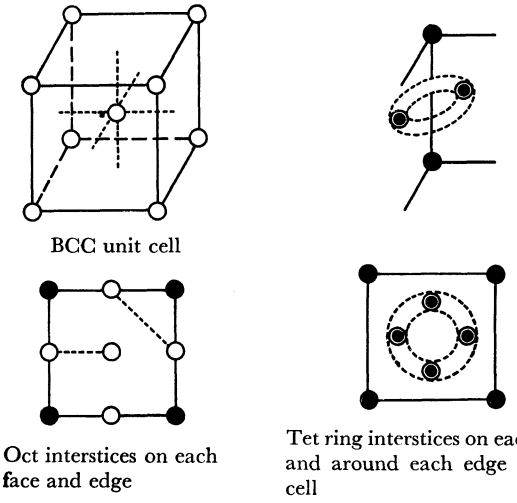


Fig. 3. Structure and location of interstices for body centered cubic metals.

stices can also be defined for BCC metals. The octahedral interstices shown in Fig. 3 are not symmetrical, *i.e.* there are 4 M^{n+} at 0.81 *a* and $2M^{n+}$ at 0.58 *a* (or *vice versa*). Such oct interstices are at centers of faces and the middle of edges of the unit cell. There are also tetrahedral interstices in the BCC structure. Tet interstices are formed by 2 body center M^{n+} and two corner M^{n+}, and 4 are located on each face at the (0,1/2,1/4) positions. Both types of interstices are joined by triangular faces of ion cores, so there is less screening of electrons by ion cores (and more volume between metal ion cores) in the BCC structure than in CCP or HCP structures. It is unlikely that both the closely spaced oct and tet interstices could be occupied by electrons. It is also expected in view of the similarity in energies of the BCC and close-packed structures that there would be the same number of interstitial electrons in BCC metals as CCP or HCP metals. Thus, the maximum number of electrons expected would be 2 electrons per face (one interstice) or two electrons per edge in octahedral interstices or 2 electrons per face in tetrahedral interstices. Any of these possibilities gives a total of 12 electrons per unit cell or 6 electrons per ion core as a maximum.

In comparing the screening of electrons by ion cores in BCC it was noticed that although both oct and tet interstices were joined' through triangular faces, the orientation of tet interstices caused the binding regions of one tet interstice to extend well into an adjacent tet interstice. This observation along with the close proximity of the tet interstices makes it likely that the binding region is continuous for tet interstices on a face (and likewise around the corresponding interstices around an edge). This would place a ring of tetrahedral interstices on each face (f. tet) and likewise a ring of interstices centered on the middle of each edge (e. tet) and perpendicular to the face tet rings. The two sets of rings are interlocking. This interstitial-electron distribution for BCC metals[17a] corresponds to the areas of negative magnetization observed in neutron diffraction studies by Shull and Mock for BCC iron. This first physical explanation of these neutron diffraction observations is discussed further in Part IV. The CCP and HCP lattices had no comparable ring structure of interstices.

The symmetry of the tetrahedral interstices in BCC as well as the freedom of motion of electrons makes it more likely that tet interstices rather that oct interstices are occupied in BCC metals. Some possible exceptions will be noted for intermetallic phases as discussed in Part V.

As seen in Fig. 3 the distances for oct interstices vary from 0.8 for two oct edge interstices and 0.58 for an oct edge and oct face. The latter interstices are not effectively screened by ion cores. The distances for the interlocking rings of tet interstices have the same distances from centers of rings as those for oct (see Table 1). The distances are larger when all the tet rings are not occupied by 1 electron each. In BCC the symmetry of face tet and edge tet is identical, so there is no preference for occupancy of either type of tet interstice in this structure (see spin restrictions below, however.)

It is inherent in the interstitial-electron model that after 3 itinerant $\bar{e}$ are present there must be pairing of electrons in the interstices, and that after 6 electrons are present there must be localization of any additional electrons on the metal ion core as *d*-electrons or "bound" electrons. It has been postulated that vacancies in interstices are necessary for metallic properties so the localization is expected after 5 electrons are present. There is an additional possibility of some localization on cores after 3 electrons as an alternative to electron pairing in interstices. For transition metals past group 5 (*e.g.*,/V^{5+}, 5 $\bar{e}$/BCC), there will be localization of *d*-electrons. The interstitial-electron model will specify location of the itinerant electrons in these metals. Since the itinerant electrons in the instantaneous picture can be considered as ligands around the metal ion core, the degeneracy of the *d*-orbitals is determined and thus the magnetic properties of the transition metal. These structures are discussed in Part IV.

The intersitial-electron model leads to formulae for the electronic structure of metals which specify the metal ion core charge and the number of itinerant electrons in octahedral or tetrahedral interstices. It will be seen below that spin restrictions limit the electron preference for oct interstices in HCP and for tet interstices in CCP with the result that electron density differences in the two types of interstices are not large. In addition to this localization of electron density according to interstice type, there can be localization within the interstice. The model postulates that there will be a maximum of electron density at the centers of interstices. In view of rapid electron motion this probably will be a very flat maximum in electron density. Postulate VIII mentions variations in electron density with occupancy and with polarization effects; these will be discussed in Part III in connection with lattice distortions and properties of metals.

4. Restrictions on Metal Electrons Due to Electron-Spin

The model defines the binding region of electrons and location of electron density as corresponding to

octahedral or tetrahedral interstices in close packed metals and to the interlocking ring tet interstices in BCC metals. When electrons are in adjacent interstices which are not well screened by ion cores (*i.e.* adjacent interstices joined by triangular faces), greater repulsion is expected when the adjacent electrons have the same spin. Thus, in keeping with the Pauli Principle, it is postulated that electrons in such adjacent interstices have opposite spins. It follows then from the model that in CCP, electrons in tet interstices have opposite spins from electrons in oct interstices. In HCP the electron spins must alternate within both oct and tet interstices and between adjacent oct and tet as well because all these interstices are interconnected by triangular faces. In BCC structures adjacent electrons in tet rings will have opposite spins. It can be seen that because of these spin restrictions there is a correlation of electron motion due to spin as well as the correlation due to $\bar{e}$ repulsions and that both are determined by the symmetry of the ion cores and interstices.

Without motion of ion cores there could be a large number of electrons in the whole metal lattice with the same 4 quantum numbers. However, the lattice vibration gives rise to a large number of small energy variations. These energy differences also allow several electrons of the same spin around a given ion core. It should be noted that the restrictions due to electron spin became more important as the total number of itinerant electrons per metal ion core increases, *e.g.* with only 1 $\bar{e}$, spins can be random in BCC. When there are more than 3 electrons there must be pairing of electrons in some interstices for all metal structures. The details of such electron distribution is discussed in Part II for each metal. It will be assumed that at normal temperatures there are sufficient energy variations of $\bar{e}$ in interstices to make the most severe restrictions of the Pauli Principle inapplicable, *i.e.* all interstices can potentially be occupied by electrons. This is discussed further in Part VI on Superconductivity. The above interpretation of the Pauli Principle is similar to that of Bader and Preston[12] who discuss the relation of electron density to the usual orbital considerations in applying the Pauli Principle. Bent[6] has used the term "Pauli Mechanics" to emphasize the importance of the Pauli Principle in chemistry.

The restrictions on interstice occupancy due to electron spin can oppose the preference for tet occupancy in CCP and oct occupancy in HCP which was based on distance of electrons and their screening from adjacent electrons by ion cores. Since there is only low paramagnetism for most metals there must be roughly equal occupancy of oct and tet interstices for CCP metals to give equal spins of each kind. The preference for tet occupancy could only be satisfied in these cases by electron pairing in tet interstices. It will be seen in Part II that this probably occurs for some metals and in Part IV that unbalanced itinerant electron spins do occur in some of the ferromagnetic metals.

In regular HCP there is alternation of spins in both tet and oct interstices, so there is essentially no restriction on occupancy due to spin. However, in the HCP structures with c/a less than 1.633 the bipyramidal intersticies are in two sets which adjoin two oct interstices in a line. For this arrangement to give opposite spins in adjacent interstices only 1/2 oct can be occupied by single electrons if all the tet are occupied. Other ratios apply when a fraction of the tet interstices are occupied.

Since so many metals are weakly paramagnetic it must be assumed that the spin restrictions are more important than the interstice preference suggested by interstice distance and $\bar{e}$ screening by ion cores.

5. Occupancy of Interstices in Metals by Electrons

The criterion as to whether an interstice will be occupied by an itinerant electron ultimately must depend on relative energies of the electrons in the metal structure. An attempt will be made to list the various factors that determine electron energies in metals and to assess the effect of each. From the interstitial-electron model the following factors are expected to influence the energies of itinerant electrons: (1). The number, symmetry, and positive field strength of M^{n+} around an interstice. (2). The distance between neighboring M^{n+} and between itinerant electrons in interstices and M^{n+}. (3). Volume available for $\bar{e}$ in the interstice. (4). Distance of $\bar{e}$ neighbors and the extent of screening by M^{n+}. (5). Spins of neighboring $\bar{e}$ and their screening. (6). Extent of pairing of $\bar{e}$ in interstices. (7). Presence of localized *d*-electrons or bound electrons on M^{n+}. (8). Magnitude of lattice vibrations.

The attraction of $\bar{e}$ due to (1) must balance the repulsions of itinerant electrons and the ion-core repulsions. Similarly, there is a balancing of effects due to potential in the interstice and the volume (3). Presence of localized *d*-electrons affect both symmetry and field of M^{n+} and must be treated as special cases (See Part IV).

When comparing metals of approximately equal fields of M^{n+} and with equal numbers of itinerant electrons the decisive factors are then the $\bar{e}$-$\bar{e}$ repulsions (determined by the screening by ion cores and distance) and spin restrictions. Thus, in the majority of metals a decision as to interstice occupancy can be made on the basis of obtaining the minimum itinerant electron repulsion while at the same time balancing itinerant $\bar{e}$ spin. This is accomplished by a maximum spreading of $\bar{e}$ through the structure in preferred interstices while also satisfying the requirement for maximum screening of ion core repulsions.

Lattice vibrations have not been discussed in relation to the interstice occupancy. The instantaneous picture which will be used to specify electronic structures always has an imbalance of electron energies, since there is greater screening of ion core repulsions in a region where the interstice is occupied by an electron than when it is vacant. A rapid movement of electrons is expected to lead to a time-average picture in which

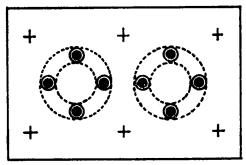
25) C. C. Shull and H. A. Mook, *Phys. Rev. Lett.*, **15**, 184 (1966).

there is electron density in all interstices. Lattice vibrations play an important role in this dynamic picture. At every change in positions of ion cores in the lattice vibration, all of the electron energies are shifted from equilibrium. Rapid movement of electrons is expected to restore equilibrium and optimum binding for the new state. As pointed out earlier the average electron density distribution in all the interstices can still retain the degree of preference for oct occupancy or tet occupancy, if this is present in the instantaneous picture of specific interstice occupancy, since the same correlation effects are in operation during electron motion.

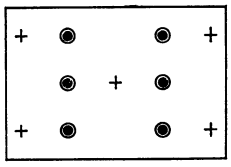
Two examples will be given to illustrate the use of the interstitial-electron model in defining the electronic structure of a metal. Sodium metal has the BCC structure, and thus two Na^+ and two itinerant electrons per unit cell. Since there is no interstice preference in BCC these $\bar{e}$ are expected to occupy 1 f.tet and 1 e.tet ring (or 2 f.tet and 4 e.tet per unit cell).

$$|2Na^+,\ \bar{e}_{f.tet},\ \bar{e}_{e.tet}|BCC$$

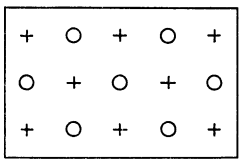
The instantaneous picture of electron occupancy can be described as having $\bar{e}$ in tet rings on upper and lower horizontal faces and $\bar{e}$ in tet rings on 4 vertical edges. There is 1/6 occupancy of interstices, and since there is not likely to be interaction of electrons so widely spread, spins can be random. In the time-average picture there is equal electron density on all faces and edges. This is shown in Fig. 4a.



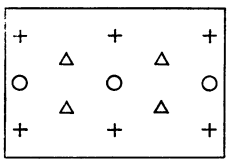
4a. Sodium Metal (100 plane)



4b. Na (110 plane)



4c. Copper Metal (100 plane)



4d. Cu (110 plane)

Fig. 4. Electron density on different crystal planes of Na and Cu metals.
(⊙=tet rings, ○=oct interstices, △=tet interstices, +=ion cores)

Copper metal has the CCP structure in which $\bar{e}$ has tet preference. However, since copper is diamagnetic, there must be balancing of spins which can come about by equal occupancy of oct and tet interstices. The structure for Cu is written for the unit cell of 4 Cu^+ and 4 $\bar{e}$:

$$|4Cu^+,\ 2\bar{e}_{oct},\ 2\bar{e}_{tet}|CCP$$

This represents 1/2 occupancy of oct and 1/4 occupancy of tet by $\bar{e}$ and the average $\bar{e}$ density is shown in Fig. 4c.

All of the metals of Groups I—V will be treated in Part II and those of Groups VI—VIII in Part IV.

6. The Interstitial-Electron Model and Metal Alloys

Metallic structures for alloys of 2 or more metals can be written in the same way as for pure metals. There will be an array of M_a^{n+} and M_b^{m+} metal ion cores with $(n+m)$ itinerant electrons in interstices. When the electric fields around the ion cores of the two metals are similar there will be no disruption of the periodic potential of the lattice, so electrons will move freely throughout the structure, and no change in metallic properties in general is expected. A general formula for a CCP alloy with equal distribution of electrons in oct and tet would be:

$$|M_a^{n+},\ M_b^{m+},\ \frac{1}{2}(n+m)\bar{e}_{oct},\ \frac{1}{2}(n+m)\bar{e}_{tet}|CCP$$

Some degree of localization in interstices would be expected as m and n are further apart or as the size of M_a and M_b differs. The variety of alloys probably results from the possibility of this kind of localization of itinerant electrons. The intermetallic phases discussed in Part V have abnormally large localizations of electron density with formation of electron pairs in certain interstices.

7. Discussion

The interstitial-electron model emphasizes the spatial distribution of electrons in metal structures. This makes it possible to consider metal properties in terms of occupied or vacant interstices, and the "degree of localization" of electrons will be useful in discussing deviations from ideal metallic behavior. The high degree of interstitial delocalization of electron density in metals contrasts strongly with the high degree of localization in a solid structure such as diamond, with electron pairs between all of the ions. The $\bar{e}$ localization in metals proposed in the interstitial electron model is more closely related to the $\bar{e}$ localization in metal cluster compounds and metal complexes than to the electron distribution in polar or non-polar molecules. It may be clarifying to relate the interstitial-electron model to other models and theories of metals.

Raich and Good[26] have proposed an electrostatic-type model for metals using uniform electron density between cores, whereas the present model proposes some degree of interstitial localization of electron density. Wannier *et al.*[13] have recently demonstrated that application of the Hellmann-Feynmann theorem to metals makes some localization of electron density necessary in metals to account for cohesion. The magnitude of this localization is consistent with that suggested in this paper and for metals discussed in Part II. Girifalco[27] has suggested the kind of wave functions possible for a localized description of electron density in metals. Hubbard[28] has made proposals for considerations of structure in the electron density.

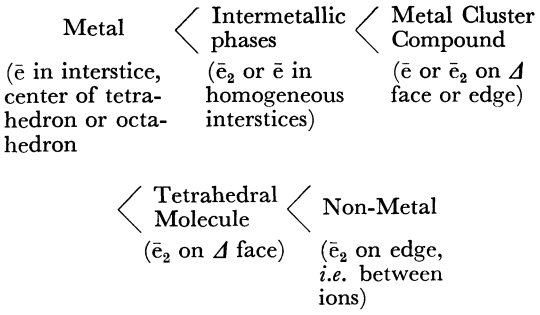
26) J. C. Raich and R. H. Good, Jr., *J. Phys. Chem. Solids*, **26**, 1061 (1965).
27) L. A. Girifalco, *Int. J. Quantum Chem.*, IIIS, 879 (1970).
28) J. Hubbard, *Proc. Roy. Soc.*, **A244**, 199 (1958).

The above authors provide some background and justification for the interstitial-electron model used in this paper. Further justification arises from purely classical considerations of electrons in metals. Harrison has pointed out that an itinerant $\bar{e}$ has its greatest velocity near an ion core, and thus spends most of its time in regions away from the ion cores. The present model defines this region as the center of interstices. Discussion of hydrogen in metal[19] places the hydrogen at the centers of interstices where there is greatest concentration of electron density. Thornber[30] has shown that "atomic" electron states are required to explain optical transitions rather than $\bar{e}$ in energy bands.

Other discussions of localized binding such as those of Pauling[31] and Engle-Brewer[32] appear to be further from band theory than the present model. It is of interest to consider how the highly successful Brewer-Engel Correlation might be related to the concepts of the interstitial-electron model. It is a possibility that the s, sp, and sp^2 (or d_xs, d_xsp, and d_xsp^2) binding proposed by Engel places electron density in spatial directions closely corresponding to the interstitial localization proposed in this paper. The orbital constructions of Trost[33] and the band structures proposed for transition metals by Goodenough[34] both emphasize the spatial extension of d-electrons in metals. The present model considers the itinerant electrons as ligands rather than the adjacent transition metal ion core, and is thus only indirectly related to the models of Trost and Goodenough. The differences will be treated in detail in the discussion of magnetic properties of metals in Part IV. The present model treats itinerant electrons in molecular orbitals (as does band theory) and not in atomic orbitals.

The method of pseudopotentials in metals[35] appears to be an extremely useful concept which has some striking similarities to the interstitial electron model. Ziman[3,36] has termed the screened ion core a "pseudo-atom". This ion core with its localized charge density interacts weakly with its neighbors. This appears the same as the manner ion cores are treated in the interstitial-electron model, and Ziman[3] emphasized that the method of pseudopotentials derives from and is entirely equivalent to band theory of metals. The "orthogonalization hole" in the method of pseudopotentials has its counterpart in the non-penetrable ion core postulated for the interstitial-electron model. The form factor[35] appears related in the two, while the structure factor in the interstitial-electron model would deal with the geometry of $\bar{e}$ in interstices rather than of the ion cores. It will be seen in Part II that the electronic structure of Al as derived from the interstitial-electron model has the same degree of localization of electron density in tet interstices as found by Harrison[35] in calculations of electron density for Al by the method of pseudopotentials. This is illustrated by data in Part II. Other models for metals in which there is some localization of electrons have also been discussed by Hubbard,[28] Cutler,[37] Szas and Mcguinn,[38] and Gombas.[39]

The concept of binding regions is useful in relating metallic binding to that in molecules and in non-metallic solids. For the tetrahedral and octahedral interstices shown in Fig. 1 and 2 there are single electrons or electron pairs in these interstices. For tetrahedral molecules, *e.g.* with 8 valence electrons, as discussed above there could be an $(\bar{e})_8$ closed shell or four electron pairs centered on triangular faces of the tetrahedron. For octahedral molecules with 12 valence electrons there can be electron pairs centered on 6 faces. There can be single electrons in these positions for metal clusters of these geometries in complexes containing metal clusters, and these can be considered intermediate between metals and polyatomic molecules. When the C.N. is low as in Silicon (diamond structure, tetrahedral arrangement), $(\bar{e})_2$ will be along edges of the tetrahedron to give the usual kind of binding in non-metallic solids, *i.e.*, electron pairs between all the ion cores. The increasing localization of electrons for these substances is as follows:



The interstitial-electron model thus treats metallic binding in the same way as other forms of chemical binding and shows that metallic binding is unique in its high degree of delocalization of $\bar{e}$ density.

The author wishes to thank the Japan Society for Promotion of Science for the invitation to Hokkaido University as a Visiting Scientist (1971—72) and to express appreciation to Professor Toya and the Staff of the Research Institute for Catalysis for valuable suggestions during Seminar discussions on this series of papers.

29) Y. Ebisuzaki and M. O'Keeffe, Ch. 5 in "Prog. in Solid State Chem.", Vol. 2, Ed. H. Reiss, Pergammon Press, London (1967).
30) K. K. Thornber, *Sci. Prog. Oxf.*, **57**, 149 (1969).
31) L. Pauling, *J. Amer. Chem. Soc.*, **69**, 542 (1947).
32) N. Engle, *Acta Metalurgica*, **15**, 557 (1966), *Powder Met. Bulletin*, **7**, 8 (1954) and earlier papers quoted there; L. Brewer, *Science*, **161**, 115 (1968).
33) W. A. Trost, *Can. J. Chem.*, **37**, 466 (1959).
34) J. B. Goodenough, *Phys. Rev.*, **120**, 67 (1966).
35) W. A. Harrison, "Pseudopotentials in the Theory of Metals", W. A. Benjamin, Inc, m New York, 1966.
36) J. M. Ziman, "Electron and Phonons", Oxford, Clarendon Press, 1968; *Adv. Phys.* **13**, 89 (1964).
37) M. Cutler, *J. Chem. Phys.*, **46**, 2044 (1967).
38) L. Szas and G. McGuinn, *ibid.*, **45**, 2898 (1966).
39) A. Gombas, *Phys. Lett.*, **24A**, 64 (1967).