CANADA

ORBITAL THEORY IN THE TRANSITION METALS

by

W. R. TROST

MINERAL DRESSING AND PROCESS METALLURGY DIVISION
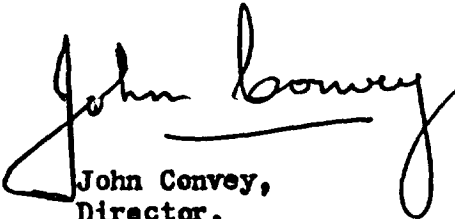
FOREWORD

This study was undertaken by Professor W.R. Trost during a year of sabbatical leave, most of which was spent at the Mines Branch, Department of Mines and Technical Surveys. It represents an attempt to account for the chemical, and some at least of the physical, properties of the transition metals in terms of orbital theory.

The demands which modern technology is making on materials, particularly metals, are increasingly severe. While it is only through an understanding of the structure of metals that we can hope to make the most of their unique properties, such an understanding has proved very difficult to come by. This theoretical study is a contribution in this field.

John Convey,
Director,
Mines Branch.

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W. R. Trost

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ABSTRACT

Orbital constructions and electron populations are worked out for the bands in the transition metals. Within the framework of the method it is possible to predict the lattice elected by the elements. Manganese and iron are exceptions, and $\propto$-Fe is treated as a special case. Numerical values for electron populations in the several s,p,d and hybrid bands, including their bonding, antibonding and non-bonding levels, are obtained.

Chemical reactions, in which binary compounds are formed, appear from specified inter-orbital reactions. Transition metal alloys (d,s,p vs d,s,p), intermetallic compounds (d,s,p vs s,p) and interstitial compounds ((n-1)d,ns,np vs 2s, 2p) are considered. Lattice-composition relationships and band populations are obtained.

The properties of the populated bands are shown to have a correspondence with some of the physical properties of the elements and compounds. Numbers are obtained for the residual and saturated moments and for the Curie point, in $\propto$-Fe.

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PART I – ORBITAL CONSTRUCTIONS AND ELECTRON POPULATIONS IN THE TRANSITION METALS

INTRODUCTION

Although molecular orbitals were first proposed for metals by Bloch (1) in 1928, the orbital constructions, and hence the electron populations, for the bands in metals (particularly for the transition metals) are still lacking. In simple cases, such as the alkali metals, detailed calculations of the binding energy have been made and reasonable agreement with experimentally determined binding energies has been obtained (2). Even in the case of atoms with one valence electron, however, the definition in space of the atomic orbitals comprising the bands is missing. In the more complicated case of the transition metals, where up to twelve valence electrons and nine atomic orbitals are to be counted for each atom, the binding energy calculations are more difficult, and the problem of locating the orbitals and electrons is also more complex. Here, it is perhaps correct to say that as yet no general success has been attained. Indeed, in many cases as a simplification the d orbitals have been ignored. It is true that Pauling counted d electrons when he proposed metallic valences for the transition metals (3), but the spatial constructions and the electron populations of the bands were not offered. Indeed, precisely because of a general lack of emphasis on the directive properties of the orbitals, it has up till now not been possible to answer the simple structural question, "Why should a particular metal have one lattice rather than another?".

It would seem that a solution to the problem is implicit in the molecular orbital theory, particularly in view of recent

developments in the ligand-field theory (4), and the work of Jaffe (5)
and of Craig, Maccoll, Nyholm, Orgel and Sutton (6,7), on orbital-pairs.

THE TRANSITION METALS

In the transition metals, nine orbitals (one ns, three
np and five (n-1)d) are to be counted for each atom. To make a metal
it is necessary to locate in space the nine orbitals of each of an
infinite number of atoms in such a way that the orientations and the
overlaps of every orbital become specified. The orbital constructions
are to place the nuclei on lattice points. At the same time, through
the overlap property, the orbital interactions that stabilize the
lattice are established.

The number of valence electrons in the transition elements
varies from three (s^2d^1) to twelve (s^2d^{10}). As bonding, antibonding and
non-bonding bands are in general to be expected from the orbital
constructions, the net binding energy, and hence the stability, of
the lattice will also be a reflection of the changing electron
populations in these bands. It therefore becomes necessary to classify
the energy levels of the several bonding, antibonding and non-bonding
bands, relative to each other, so that the valence electrons can be
placed and the populations in the bands calculated. That is, both
electron density and orbital overlap become criteria for lattice
stability.

THE ORBITAL CONSTRUCTIONS OF THE BANDS

The overlaps and symmetry relationships as between pairs
of s, p and d orbitals have been worked out in detail by several
authors (5,6,7) and are summarized in Figure 1. Removal of the
restriction that the number of orbitals in overlap be limited to two,

permits more closely packed assemblies of these orbitals to be sought.
When all orbitals have been so arranged, and consideration given to the
numbers of electrons involved, lattice systems that reproduce the
metallic lattices are obtained. The d,p and hybrid orbitals become the
orbitals that determine structure. The spherical s orbital, having no
directional dependence, offers no choice between alternative close-
packed structures.

1. The p orbitals

The shape and the degeneracy of the orbitals provide a
basis for choosing among alternative close-packed schemes. The p orbital
construction shown in Figure 2, in which each p orbital overlaps eight
others, has three advantages. The arrangement can be indefinitely and
smoothly expanded, as more orbitals are added, to produce an indefinitely
large and perfect body-centered cube. The arrangement has a three-fold
degeneracy, as the three mutually perpendicular directions are equivalent
with $p_x(p_x)_8 = p_y(p_y)_8 = p_z(p_z)_8$. That is, the three p orbitals on
each atom overlap the corresponding orbitals on the adjacent eight
atoms in the same way. Finally, as an assurance that the overlap
factor for the arrangement is favorable, the distance between the
centers of the overlapping lobes is 0.81 of the internuclear distance.

The result is that what will be called the bcc p band has
cubic symmetry, is perfectly degenerate in the three p orbitals, is
delocalized over all atoms in the lattice, and constitutes a close-
packed assembly of p orbitals.

2. The d orbitals

When we turn to the d orbitals, it at once becomes evident
that the degeneracy of the sub-shell cannot be retained in metallic

bonding unless hybridization occurs, as all d orbitals cannot achieve the same overlap at the same time in any one lattice. The symmetry relationships for space packing, however, separate the sub-shell into two groups of orbitals, the diagonal (d_{xy}, d_{xz}, d_{yz}) and the axial (d_{x2-y2}, d_{z2}). Two different close-packed structures are possible for the diagonal orbitals. In the first of these, shown in Figure 3, one orbital overlaps eight others. This configuration has the merit that each diagonal orbital becomes identically engaged, so that $d_{xy}(d_{xy})_8 = d_{xz}(d_{xz})_8 = d_{yz}(d_{yz})_8$, thereby preserving the degeneracy of the three orbitals and establishing a body-centered cubic lattice. In it the d band is delocalized over all atoms. The interlobar distance, in this construction, is 0.58 the internuclear distance, a favorable feature for overlaps that is at least partly counterbalanced by the manner of approach of the orbitals. This is through the thickness of the lobes, much as in the d-d δ bonding of Figure 1, which is not in the direction of maximum extension. The band will be called the bcc dϵ band to conform with usage in the ligand-field theory (4). (The dϵ level has also been called t_{2g} and $\gamma 5$.) The two remaining orbitals, d_{x2-y2} and d_{z2}, constitute the dγ level.

A second way to close-pack d orbitals, shown in Figure 4, places four orbitals around a central one. When the three diagonal orbitals on a central atom are so engaged, twelve atoms surround the central one, in a cubic close-packed arrangement, that is, $d_{xy}(d_{xy})_4 = d_{xz}(d_{xz})_4 = d_{yz}(d_{yz})_4$, so the cubic close-packed dϵ band, like the body-centered cubic dϵ band, has cubic symmetry and is delocalized over all atoms. In each arrangement (i.e. bcc dϵ and ccp dϵ), two d orbitals are still to be located. In both lattices, the

direction of maximum extension of the $d\gamma$ orbitals ($d_{x^2-y^2}$, d_{z^2}) is identical with an octahedral arrangement of next nearest neighbors. The distance between the next nearest neighbors, as compared with the nearest neighbor distance, is 1.15 in bcc and 1.42 in ccp. In orbital constructions like that of Figure 4 (for $d_{x^2-y^2}$; d_{z^2} has its maximum extension on the z axis), these internuclear distances enable bcc $d\gamma$ to make a substantial minor contribution to the bonding[1], whereas ccp $d\gamma$ is virtually non-bonding. The bcc $d\gamma$ will therefore support bcc $d\epsilon$ when fewer than five d electrons are present, but will weaken bcc $d\epsilon$ when more than five electrons are present. In the latter case, as antibonding levels in bcc $d\gamma$ become occupied, the cubic close-packed lattice with a ccp $d\epsilon$ band becomes preferred.

3. Hybrid orbitals

Two hybrid orbital constructions lead to close-packed lattices. One of these applies to ground states between d^3 and d^7, which is just the gap left when orbital constructions based on the $d\epsilon$, $d\gamma$ split are employed. The second hybrid construction becomes relevant when the d sub-shell begins to be non-bonding, as in $s^2 d^{10}$.

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1. In view of the somewhat different shapes of the two orbitals, it is possible that $d\gamma$ is not perfectly degenerate. A detailed analysis shows, however, that these orbitals also have small overlaps with nearest neighbors (the overlaps are small because of the orientations and shapes of the orbitals) which tend to make the two bonding functions equivalent. Therefore, although the band cannot be considered solely a next-nearest neighbor band, it is possibly correct to describe it as a weakly bonding band with two-fold degeneracy. It is also assumed, in ligand-field theory (4), that d_{z^2} and $d_{x^2-y^2}$ remain degenerate in the $d\gamma$ level.

The only hybrid sets that use four and five d orbitals and lead to close-packed structures are sd^{4}p and d^{5}p. In both of these 1x6 configurations, the bonding directions are toward the corners of a trigonal prism (8). When a set of identical atoms in this state is brought together a hexagonal close-packed lattice results, in which each atom is bonded to six neighbors through localized bonds but is equidistant from twelve, as shown in Figure 5. The orbitals remaining after sd^{4}p or d^{5}p is chosen are, accordingly, to be placed with reference to the hcp system.

The last arrangement to be described is an sp^2 construction. The packing of sp^2 orbitals as in Figure 6 sets up close-packed layers of atoms. The layers are bonded to each other through the p_z orbital, which provides a $p_z(p_z)_6$ band, and by a perpendicular delocalization in the three-center sp^2 molecular orbitals. A distorted hexagonal close-packed lattice appears, with six nearest neighbors in a layer, and three more distant ones above and three below. The electron cloud of the p_z band extends over the lattice but contains regularly spaced vacancies that have a definite shape. The superimposed sp^2 molecular orbitals attain, through delocalization, the shape of an endlessly repeated hour-glass, with the thin part of the electron cloud between the layers and the thick part in the layer. The sp^2 band consists of an indefinite array of these, in parallel extension in a 1x6 packing, with each endless hour-glass precisely occupying a vacancy in the electron cloud of the p_z band.

THE ATOMIC ORBITAL ENERGY LEVELS

An explanation of the properties of the transition metals should take account of both the spatial and the energy level properties of the orbitals. The foregoing consideration of the spatial problem gave rise to specific band systems with orbital constructions requiring one or another of four lattices, the body-centered cubic, the hexagonal close-packed, the cubic close-packed and the distorted hexagonal close-packed. The energy level problem involves a consideration of both the atomic and molecular orbital energy levels. Complications arise here because of the likelihood that these levels change as the d sub-shell fills; as the principal quantum number varies; and, in the molecular orbitals, as the band systems change. The atomic orbitals will be dealt with first.

An inspection of the ground states of the transition elements shows that the energy level of the (n-1) d orbitals, which at first is above that of the ns orbital, as in s^2d^0, changes value until it is the stabler orbital, as in s^0d^9 and s^0d^{10}. This cannot be thought of as simply a regular increase in the stability of the d orbital as the d sub-shell fills, for energy is also contributed to the system in a non-linear way. Because of a lower electrostatic repulsive energy and a more favorable exchange energy among single electrons with parallel spins, states with the maximum number of singly filled orbitals are favored, as is well known from Hund's rule (4). As the magnitude of this energy term depends|directly on the number of singly filled states, the d orbitals will be stabilized by increasing amounts as the number of valence electrons increases from one to six. Such a change is shown in the ground states of these

atoms.

Valence electrons	Ground states
1	$s^1 d^0$
2	$s^2 d^0$
3	$s^2 d^1$
4	$s^2 d^2$
5	$s^2 d^3$, $s^1 d^4$
6	$s^2 d^4$, $s^1 d^5$

The number of single electrons, and hence the magnitude of the exchange energy contribution, must necessarily diminish upon the addition of further electrons. This will make the d levels fall more slowly after the six-electron atom than before it. However, the linear factor, associated with the increasing positive charge on the nucleus, still persists. The d levels are stabilized more than s because the (n-1)d electrons are, on the average, closer to the nucleus than the ns. The d levels are therefore more directly affected by the increasing electrostatic field of the nucleus. At the same time, the (n-1)d electrons intervene between the nucleus and the spherical electron cloud of the ns orbital. A screening effect occurs that tends to make the s electrons somewhat unresponsive to an increase in the charge on the nucleus. Both effects foresay a steadily increasing relative stability in the d orbitals as the sub-shell fills. This can also be seen in the ground states of the elements.

Valence electrons	Ground states
7	s^2d^5, s^1d^6
8	s^2d^6, s^1d^7
9	s^2d^7, s^1d^8, s^0d^9
10	s^2d^8, s^1d^9, s^0d^{10}
11	s^1d^{10}
12	s^2d^{10}

It is to be noticed that the d levels are unambiguously below the s level for the first time in the ground state, s^0d^9.

When the effects of filling the sub-shell are combined with the stabilizing property of single electrons in the sub-shell, a two-part curve as in Figure 7 is forecast, which shows the change in the relative values of the energy levels as the number of valence electrons increases. In drawing Figure 7 it was assumed that the d passes through the s level at six valence electrons (s^1d^5), and that d is just below p at three valence electrons (s^2d^1). As a simplification, the two parts of the d curve were drawn to repeat each other.

THE METALLIC BANDS

For an adequate description of the bands in a metal, in addition to the energy levels of the atomic orbitals and the orbital construction of the bands, it is necessary to know the binding energy and the density of states in the molecular orbitals that comprise the bands. Delocalized, localized, antibonding, and non-bonding bands are to be considered.

1. The delocalized bands

Bands in which electrons are delocalized over all atoms have been constructed from s, p and d orbitals and, with a more limited delocalization, from sp^2 orbitals. These delocalized bands are specific cases satisfying the principal conditions for the classic Bloch molecular orbitals (1). The width of the bands, which is the separation between the lowest and the highest state in the band, and the level of the lowest lying state are to be obtained.

It is convenient, though not entirely correct (see later for a rule of thumb), to assume that the density of states is uniform in delocalized bands made up of overlaps from among nearest neighbors. The phenomenon of width in the band arises from the delocalization property. As the wave function for each electron extends over all nuclei incorporated in the delocalized wave function, and as no two electrons can be identical, successive electrons must lie in states that are distinguishable in the energy parameter. Consequently, the density of states has a relation to the effectiveness of the delocalization property. In the multiple overlaps encountered in the prescribed orbital constructions, delocalization is measured both by the number of overlaps an orbital has and by the magnitude of the overlap volume. The bands made up from orbitals in close-packed arrangements can be expected to be somewhat similar in both these regards. For the d orbitals it may be recalled that delocalized bands were found among both nearest neighbors (bcc $d\varepsilon$ and ccp $d\varepsilon$) and next nearest neighbors (bcc $d\gamma$ and ccp $d\gamma$). In these cases of nearest and next nearest neighbor bands, both the density of states and the binding energy must vary, with internuclear distance as the

most direct parameter.

In detailed calculations (2) for the alkali metals, it has been shown that both s and p states are populated in Li and Na. As there is only one valence electron in these metals, it is necessary to conclude that upper states in the s band lie above lower states in the p band. Using the assumption of uniform density of states and remembering the three-fold degeneracy of the bcc p band, an electron population chart as in Figure 8 can at once be drawn. The separation between the s and p band heads, which is the only independent adjustment, has been arbitrarily chosen so that the s and p band populations become 0.775 and 0.225 electron respectively. Counting the degeneracy, this amounts to 0.775 and 0.075 electron per orbital for the s and p orbitals respectively. This arbitrary decision is not unimportant. For it, along with the assumption of uniform density of states, at once defines the energy separation between s and p atomic orbitals in units of the width of a nearest neighbor delocalized band. This can be seen by comparing the ordinates of Figures 7 and 8. Specific population figures did not appear in the calculations for the alkali metals referred to above. Pauling (9) has used the value 0.1 for the p orbital population in Li. A somewhat larger value was chosen here in the expectation that the energy separation between the atomic orbitals decreases as the principal quantum number increases. Such a trend would require a more important p orbital participation in the heavier alkali metals than in Li.

2. The localized bands

Band systems that retain more than a three-fold degeneracy in the d orbitals set up an hexagonal close-packed lattice. In this

lattice, both the d^4sp and d^5p hybrid configurations gave rise to orbital-pair overlaps between nearest neighbors, with the result that the bonding electrons became localized on pairs of nuclei. As in the ordinary convention for electron-pair covalent bonds, these spatially independent states are here assumed to be without appreciable effect on each other. That is, all such states exist at the same energy level. For purposes of definiteness, the discrete energy levels of the d^5p and of the sd^4p bands have been taken from the weighted average of the energy levels of the band heads of the delocalized s,p,d bands. The decision, in so far as its correctness is concerned, could affect electron population calculations only in the case of one modification of the six-electron atom, Table 1 (on page 26).

It should perhaps be mentioned that in another hybrid construction, that of the sp^2 configuration in a distorted hexagonal close-packed lattice, a localization property also appears when the electron population is equal to or in excess of 0.66 electron per orbital. Then bonding electron pairs can be associated with nuclear triads. The electron population was less than 0.66 per orbital in the twelve- (or two-) valence electron atoms considered here.

3. The antibonding and the non-bonding bands

The antibonding bands are identified with the corresponding bonding bands through the assumption of uniform density of states, and through the requirement that the binding energies of the bonding and antibonding states be equal and opposite. For electron population purposes, the bonding and antibonding bands then become a single system of uniformly separated states, divided into equivalent bonding and antibonding portions by the energy level of the non-bonding

atomic orbital. This can be seen in the electron population chart Figure 9, where bonding ($d\varepsilon$, $d\gamma$) and antibonding ($d\varepsilon'$, $d\gamma'$) bands are shown.

The symmetrical disposition of the bonding and antibonding states about the level of the non-bonding atomic orbital includes two variations that have a general significance. One points up the distinction to be made between nearest and next nearest neighbor bands; the other corresponds with a transition from localized to delocalized bands. Either the binding energy can decrease, which tends to compress the bonding and antibonding bands into a narrower region about the non-bonding level; or, if a decrease in delocalization occurs, both bonding and antibonding bands are compressed away from the non-bonding level towards their own lower and upper states, respectively. In each of these cases, the density of states is altered, though in the same way in both bonding and antibonding bands.

The next nearest neighbor bands, bcc $d\gamma$, ccp $d\gamma$ and hcp d_z, with internuclear distances of 1.15, 1.41 and 1.62 respectively, provide an example in which binding energies progressively decrease, compared with nearest neighbor bands like bcc $d\varepsilon$ and ccp $d\varepsilon$, where the internuclear distance is unity. In view of the decrease in binding energy, the density of states must necessarily increase as the internuclear distance increases, conceivably until, when the internuclear distance is large enough, the atomic orbital is non-bonding and single states are achieved. By associating the levels of the band heads with the internuclear distance, the density of states in bcc $d\gamma$ becomes twice, in ccp $d\gamma$ five, and in hcp d_z ten times that in nearest neighbor bands. As bcc $d\gamma'$ attains no

antibonding population, for the lattice becomes unstable before antibonding electrons appear, the decision affects antibonding electron populations only in the eight- and nine-valence-electron elements. hcp d_z' and ccp $d\gamma$' absorb the first antibonding electrons. Once these bands are filled, creating in conjunction with hcp d_z or ccp $d\gamma$ the equivalent of one or two filled non-bonding d orbitals respectively, the question of the density of states in bands with different binding energies no longer affects the population figures.

A change in the delocalization factor may also occur more gradually than is implied in the assumption of the two extremes of delocalized and localized bands. This is already indicated in the appearance of orbital constructions in which single orbitals overlap varying numbers of others (as, for example, eight in bcc $d\epsilon$, six in the distorted hcp p band and four in ccp $d\epsilon$, compared with one in a localized bond) while still retaining the delocalized property. If delocalization were subject to such a continuous diminishment, its effect on the electron population figures would be real, though small, and found mostly in the 8-, 9-, and 10-electron atoms. If, for example, ccp $d\epsilon$ and ccp $d\epsilon$' (because of the four coordination in their orbital constructions) were to some extent compressed away from the non-bonding level, while bcc $d\epsilon$ and bcc $d\epsilon$' (with eight coordination) were not, minor changes in the population of the antibonding ccp $d\epsilon$' would result. The largest effect occurs when the ccp $d\epsilon$' band is just beginning to be occupied, as in atoms with nine valence electrons, the correction tending to eliminate itself as more electrons are added.

The antibonding levels associated with the localized bonding orbitals achieve no significant population. It is therefore not necessary to specify them closely at this time.

THE FOUR LATTICES

The methods that have been outlined assume to predict both the lattice a transition element elects, and the electron population of the bands in that lattice. The predicted and the known lattices can be compared at once. Experimental values for electron populations are, however, not available, so the validity of the calculated populations cannot be properly assessed. In what follows a few words will be said about each metallic lattice.

1. The body-centered cubic lattice

The band system for the body-centered cubic lattice consists of an s band, a p band (Figure 1), and two d bands. The bcc d ϵ band has three-fold degeneracy, and begins at a lower level than the bcc d γ band, which is a next nearest neighbor band, with two-fold degeneracy.

In atoms with one valence electron, the electron population is confined to the s and p bands, Figure 8. With an increase in the number of valence electrons, not only must more electrons be placed, but the energy level of the d orbitals fall relative to the s and p as shown in Figure 7. In atoms with five valence electrons, the d orbitals may be fairly said to dominate the structure, holding 3.08 of the five electrons, Table 1 and Figure 10. The important changes that occur in the band system as the valence electron count increases from three to six are the disappearance of a small antibonding population, a regular increase in the d ϵ population, and a relatively more rapid

increase of the electron density in the d γ band. These features combine to give the lattice its limited stability range.

It is evident that in any band system the upper levels make a smaller contribution to the binding energy than do the lower states. Moreover, in systems in which the band pattern changes because of changes in the symmetry of the orbital constructions, it follows that maximum binding energy, and consequently a stable lattice, corresponds with those constructions that provide a maximum population in the low lying states. It is suggested, as a rule of thumb for these multiple overlap systems, that a stable lattice corresponds with an electron density of $2/m$ in the bonding orbitals. Here m is the number of lobes (not orbitals) in mutual overlap.

The rule of thumb may have some validity as a delocalization factor, though it is not in this sense that it will be applied. As a generalization of the delocalization observed in lone pairs and covalent bonds where m, the number of lobes that overlap, is 1 and 2 respectively, the electron density is 2 and 1 as is in each case required by the rule of thumb. In application to the multiple overlap systems, with n equal to 5 in the p band, 3 in the bcc d ϵ band and 2 in the ccp d ϵ band, the rule-of-thumb electron densities become 0.4, 0.66 and 1.0 respectively. In so far as it has significance as a delocalization factor, the rule of thumb implies that the density of states in the respective bands differs in such a way as to make their lattice constructions stable, as compared with alternate arrangements, at the prescribed electron density. If this is the case, the rule of thumb describes a limitation to the assumption of uniform density of states in the delocalized bands.

It will actually be used, however, in a rather more rough and ready sense than this, in what follows. In any event, it should be noted that the rule of thumb does not apply, as an indicator of lattice stability, to the s orbitals, for this band does not determine structure.

Both the bcc d ε and the ccp d ε orbital constructions can be applied to atoms with 3 , 4 , 5 or 6 valence electrons. The differences in the electron population charts for the two lattice systems, at any rate under the present assumptions, are entirely due to the difference, not in bcc d ε and ccp d ε , but in bcc d γ and ccp d γ . As bcc d γ (at 1.15 the internuclear distance) provides more binding energy than ccp d γ (at 1.41 the internuclear distance), the bcc d γ band begins at a lower level. The effect of this is to increase the total number of d electrons lying at low and intermediate levels in the bcc bands, as compared with ccp, where the uppermost energy levels would have to be occupied as well. The concentration of electrons in the stabler states occurs whenever the bcc d γ band shows a population which is in the 4-, 5-, or 6- valence electron atoms (Table 1). Consequently, the bcc lattice can be chosen over the ccp lattice, unambiguously only for the 4-, 5- and 6- electron atoms. The overall result is that the bcc d γ band keeps the electron density of the bcc d ε band in the vicinity of 0.66, which is the rule-of-thumb density for bcc d ε (0.34, 0.56, 0.73 and 0.92 are the calculated values for the 3-, 4-, 5- and 6- electron atoms, respectively). The electron density in the p band is also close to the 'best' value, 0.4, except in the 6- electron atom (0.32, 0.34, 0.31 and 0.22 in the 3-, 4-, 5- and 6- electron atoms, respectively).

There is no d γ population in the 3- electron atom. It

is therefore not possible to make a choice between the bcc and ccp lattices for this element on the proffered grounds. Moreover, the antibonding population appearing when bcc is elected (Table 1), and the relatively small d population, together indicate that the band system for the 3- electron atom is apt to be different in detail from those of the other transitional elements. However, a close-packed metal can evidently be obtained.

A d band population of 4.54 electrons is found in the bcc system for the 6- electron atom. Of this, 1.68 electrons are in the relatively weakly binding $d\gamma$ band. The result is that at this stage a concentration of electrons is beginning to build up in the less stable upper levels of the d band. This is to be expected as the principal d band has only three-fold degeneracy, and at least four d electrons are available for bond formation. Instability features are also shown in the deviation of the p and d band electron densities from the rule-of-thumb values. However, when the alternate band system for the 6- electron atom, which employs a hexagonal close-packed lattice, is charted, an instability feature also appears in it. The d^5p band, a system of localized electrons, is incompletely occupied, Table 1. It is therefore necessary to predict that an atom with 6 valence electrons will show two forms, one with a bcc, the other with an hcp lattice. The predictions therefore are that transition elements with 4,5 and 6 valence electrons have a bcc lattice, as is in fact the case for β Ti, β Zr, V, Cb, Ta, α Cr, Mo, and α W.

2. The hexagonal close-packed lattice

The hexagonal close-packed lattice emerges as a consistent choice for elements with 6,7 or 8 valence electrons,

although the band systems that establish the lattice are subject to minor variations within this group. With both sd^4p and d^5p providing trigonal hybrids, either configuration will establish an hcp lattice. The difference between the two will therefore be small, depending, for the most part, on whether an s band (with d^5p) or, a d_z band (with sd^4p) is to be found in the lattice. The p band is doubly degenerate in either case, though a third alternative, that of a delocalized sp^2 band (in connection with d^5p), is also possible. These three possibilities correspond to rather slight changes in the overall electron population picture, being confined to minor variations in the electron density and direction dependence properties of the conductivity bands. In no case is the lattice affected, at any rate with respect to its classification as hcp. The electron population calculations, Table 1, were made for d^5p in the case of the 6- electron atoms, and for sd^4p for the 7- and 8- electron atoms.

In addition to the appearance of localized bands, an important antibonding population also appears for the first time in this group of elements. The precise value of this population depends on the level selected for the d_z band which, like bcc $d\gamma$ and ccp $d\gamma$, is a next nearest neighbor band. The distance in d_z is 1.6 the nearest neighbor distance, so that the band would be expected to be less effective than either of the $d\gamma$'. The antibonding population is confined to the d orbitals and, under the assumptions used, is not quite equivalent to having an electron pair in a non-bonding d_z2 orbital in the 8- electron atom. In the latter case, the net bonding electrons would be lowered from 7.0 to 6.0. The prediction of an hcp lattice for the 6-, 7- and 8- electron atoms is borne out in the

elements Mo, Te , Re, Ru, and Os. Manganese and iron are
exceptions and will be referred to again.

3. The cubic close-packed lattice

Atoms with 9, 10 and 11 valence electrons satisfy the
conditions for the ccp band system, Figure 9. The transformation to
the ccp lattice occurs when an extra electron is added to the hcp system.
The ninth electron, going into the antibonding d levels of the hcp
system, would produce the near equivalent of two filled non-bonding
d orbitals in that system. As a result, neither d^5p nor sd^4p can be
constructed, and the hcp lattice is destroyed. At 9 electrons in the
ccp system, the d γ band is nearly non-bonding, and becomes so at
10 electrons. The ccp d ε remains, and with an electron density of 1
electron per orbital, provides the d orbital contribution to the
binding energy and determines the structure.

The antibonding levels that are occupied as electrons are
added to the ccp system are altogether in the d orbitals, with the
increase for the most part to be found in the triply degenerate ccp
d ε' band. That is to say, the bonding s and p and the antibonding d
levels have approximately the same energy throughout this triad. The
overall result, going from 9 to 11 electrons in the ccp system, is to
steadily diminish the net contribution of the d orbitals to the
binding energy and the lattice. At 12 electrons, the d orbitals
have become altogether non-bonding, with 3 electrons in d ε'
balancing 3 electrons in d ε. Counting the non-bonding, d γ',
the non-bonding d ε now restore a five-fold degeneracy to the d
orbitals. That is to say, at 12 electrons, the d sub-shell has become
a part of the inner core. The prediction of a cubic close-packed

lattice for 9-, 10- and 11- electron atoms is observed without exception in these elements, namely β Co, Rh, Ir; Ni, Pd, Pt, Cu, Ag, Au. The fact that α Co is hcp will be mentioned again.

4. The distorted hexagonal close-packed lattice

As described above, the 12- electron atom (speaking in valence terms) becomes a 2- electron atom, as the d levels are fully occupied and non-bonding. The band system projected for the 12- electron atom (Figure 11) is therefore in principle also applicable to the 2- electron elements, Be and Mg. The only differences to be expected are those that can be associated with the principal quantum number. This band system is, however, incompatible with the 2- electron elements, Ca, Ba and Sr. These elements have vacant d levels, which by taking electrons away from the sp^2, p bands, permit quite different electron distributions and orbital constructions. It is therefore correct to predict a distorted hexagonal close-packed lattice for Be, Mg, Zn and Cd, as is observed. It is also correct to predict that Ca, Ba and Sr will not have the same distorted hcp lattice. (Ca, Sr and Ba have cubic lattices.)

DISCUSSION

When the antibonding population is subtracted from the bonding population, a figure giving the net number of bonding electrons is obtained (Table 1). Since this number sums up only the electron populations of the several bands, and since the properties and electron dependencies of the bands differ, the number of net bonding electrons by no means shows all the significances of the band systems. For example, if the property of plasticity were to be judged from changes in overlap accompanying nuclear displacements that do not alter inter-

nuclear distances, the s band would be plastic and the d bands hard.
Moreover, as the overlaps are different in character in the
different d bands, the band populations do not always correctly
evaluate the relative magnitude of even so specific a property.
As another example, the p band has consistently the lowest ionization
potential and the lowest electron density (about 0.33 electron per
orbital) and may for these reasons be principally responsible for the
properties of conductivity and paramagnetism in these metals. Never-
theless, other delocalized bands may on occasion also make important
contributions to these two properties, as, for example, the d bands
in the 5- electron atoms.

In a more general way, as well, numbers for net bonding
electrons have less significance than the itemized list of their
parts. This arises from the condition that in band systems electrons
occupy successive levels and do not therefore all make the same
contribution to the binding energy. This is possibly of most
importance when the antibonding levels are just beginning to be
occupied (the 7-, 8- and 9- electron atoms). As the lowest levels
of both bonding and antibonding bands are filled first, the
contributions to the binding energy of a bonding and an antibonding band
exactly cancel only when both bands are fully occupied. When the
antibonding band is not completely full, it still cancels out a
numerically equivalent population. To be correct from the binding
energy point of view, however, the upper, more weakly binding states
in the bonding band are the ones to be selected. That is, the
stablest states remain and give a binding energy contribution that is
underemphasized in a number that by implication describes average

electrons.

Whatever their deficiences, it is nevertheless these numbers for net bonding electrons that have the simplest correspondence with the concept of a numerical valence. They are therefore to be compared with the metallic valences proposed by Pauling (3) for the transition elements:

Valence electrons	1.	2	3	4	5	6	7	8	9	10	11	12
Pauling's Valence	1	2	3	4	5	6	6	6	6	6	5.5	4.5
Net bonding electrons	1	2	3	3.9	5	6	7	7	4.6	3.8	3.0	2.0
Integral Valence	1	2	3	4	5	6	7	6	5	4	3	2

It is evident that agreement is good until elements with an important antibonding population are encountered. In atoms with 7 or 8 valence electrons, the very weakly binding d_z band is being occupied. As it holds 0.6 and 1.0 binding electrons in the two elements respectively, the number 7 rather overestimates the effective situation. Also, in the atoms with 9 and 10 valence electrons, rather more than a justifiable weight is given to the antibonding population in ccp $d\mathcal{E}'$, as has been mentioned; this cannot have a greater effect than to provide values for an 'average' valence of 5.0 and 4.0 for these elements respectively. In brief, the concept of an integral valence can in fact be justified as a reasonable approximation to the net bonding electron values, as shown above. Even with such adjustments to average values, a significant departure from the metallic valences proposed by Pauling for atoms with 9 , 10 , 11 and 12 valence electrons still remains. As additional support for the net bonding electron values presented in this report, their correspondence with conventional chemical valences for these elements may be pointed out.

Moreover, the physical and chemical relationships that are evident in the series of elements, Be, Mg, Zn and Cd, strongly suggest divalent atoms throughout.

Lattice structures and band populations are the predictions made in this paper. Factual comparisons are possible for the lattices, but band populations have not been measured. Even in the comparison that is possible some ambiguity remains. For it is conceivable that a specific lattice, and particularly a close-packed one, can be set up from more than one set of orbital constructions, as was indicated in the case of the hexagonal close-packed lattice. Agreement with respect to the lattice does not, therefore, necessarily prove the correctness of the orbital constructions. The corollary is also ambiguous. If a lattice is incorrectly predicted for one member of a family, it does not necessarily follow that the orbital constructions are wrong for the other members, though they must of course be wrong in the specific case.

Of the thirty transition elements, the lattices of Mn and Fe (and Hg) were incorrectly forecast. This deviation from expectations corresponds with the appearance of the property of ferromagnetism in the transition elements and may therefore have a somewhat special significance. The assumption, implied by the application of the population figures to all elements in a sub-group, that the relative levels of the ns, np and (n-1)d atomic orbitals are independent of n, is certainly not altogether correct. A general expectation is that the separations become smaller as n becomes larger. Secondly, the overlaps in the n type and (n-1) type bands are apt to have different magnitudes, even among near neighbors. This has a direct bearing on the binding energies and also on the density of states if the bands are delocalized. It is

known that the ratio of the radii of the (n-1) to the n shell has its smallest values in the first transitional period, and in that period the minimum occurs at Fe. Taken together, these two factors, the decreasing separation between the atomic orbital energy levels and the increasing relative radius of the (n-1) d orbitals as n increases, imply that the (n-1) d orbitals become consistently more important to the binding energy with larger values of the principal quantum number. This accounts for the singular observation that the melting and boiling points of transition metals (with 4 to 10 valence electrons) invariably increase, while the melting and boiling points of non-transitional metals invariably decrease, with increases in n (atoms with 3 and 11 valence electrons are intermediate in this respect; Zn, Cd and Hg fall into the non-transitional group with Be and Mg).

As it happens, the impact of what might be called these n-type variations has its maximum effect precisely at the elements Mn, Fe and Co. Moreover, as the antibonding d bands are here just beginning to be occupied, the disposition of bonding and antibonding electrons will at the same time be most responsive to these changes. That is, both the cause and the response to the cause are maximal at Mn, Fe and Co, among the transition elements. The problem becomes therefore to relocate the orbitals in these elements as specific cases (Fe has four lattices, Mn three, and Co two) and discover thereby, in the particular instances of $\propto$ Fe and $\propto$ Co, the location and properties of the ferromagnetic orbitals, presumably resident in the (n-1)d band.

TABLE 1

Electron Populations in the Bands of the Transition Elements

Element		Band Populations							Valence
Valence Electrons	Lattice System	Bonding					Anti-bonding bands[4]	Non-bonding bands[5]	net bonding electrons
		s band	p band[1]	d band	d or d_z band[2]	hybrid bands[3]			
1	bcc	0.775	0.225						1.0
3	bcc	1.00	0.96	1.02			0.02		2.96
4	bcc	1.00	1.02	1.69	0.24		0.05		3.90
5	bcc	1.00	0.92	2.18	0.90				5.00
6	bcc	0.92	0.66	2.76	1.68				6.00
6	hcp	0.12				5.88			6.00
7	hcp		0.37		0.63	6.0			7.00
8	hcp		0.50		1.0	6.0	0.50		7.00
9	ccp	0.97	0.81	3.0	2.0		2.21		4.57
10	ccp	0.99	0.89	3.0			1.12	4.0	3.76
11	ccp	1.0	1.00	3.0			2.00	4.0	3.00
12 dis.	hcp		0.33			1.67		10.0	2.00

[1] Three-fold degeneracy in cubic lattices; two-fold in hcp; one-fold in distorted hcp.
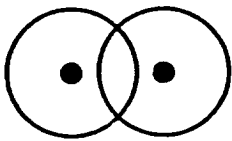
[2] $d\gamma$ and d_z are next nearest neighbor bands in cubic and hexagonal systems respectively.

[3] sd^4p for 6 electrons; d^5p for 7 and 8; sp^2 for 12.

[4] s' for 3 and 4 valence electrons; d_z' for 8; $d\varepsilon$' and $d\gamma$' for 9 (see Figure 9).
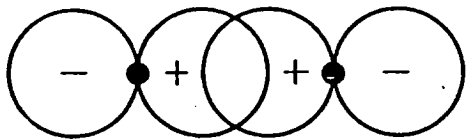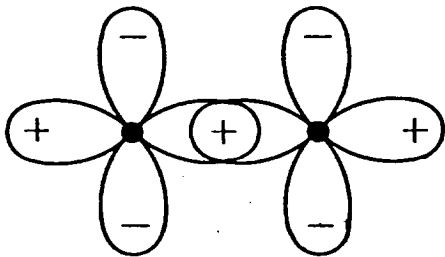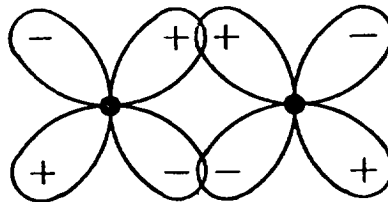
[5] $d\gamma$ for 10 and 11 valence electrons; d^{10} for 12.
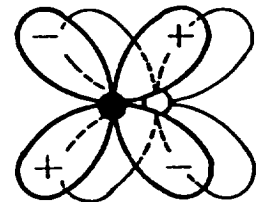
σ π δ

s-s σ

p-p σ

p-p π
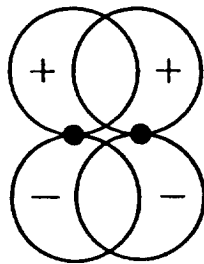
● ATOM ABOVE

○ ATOM BELOW

d-d σ d-d π d-d δ
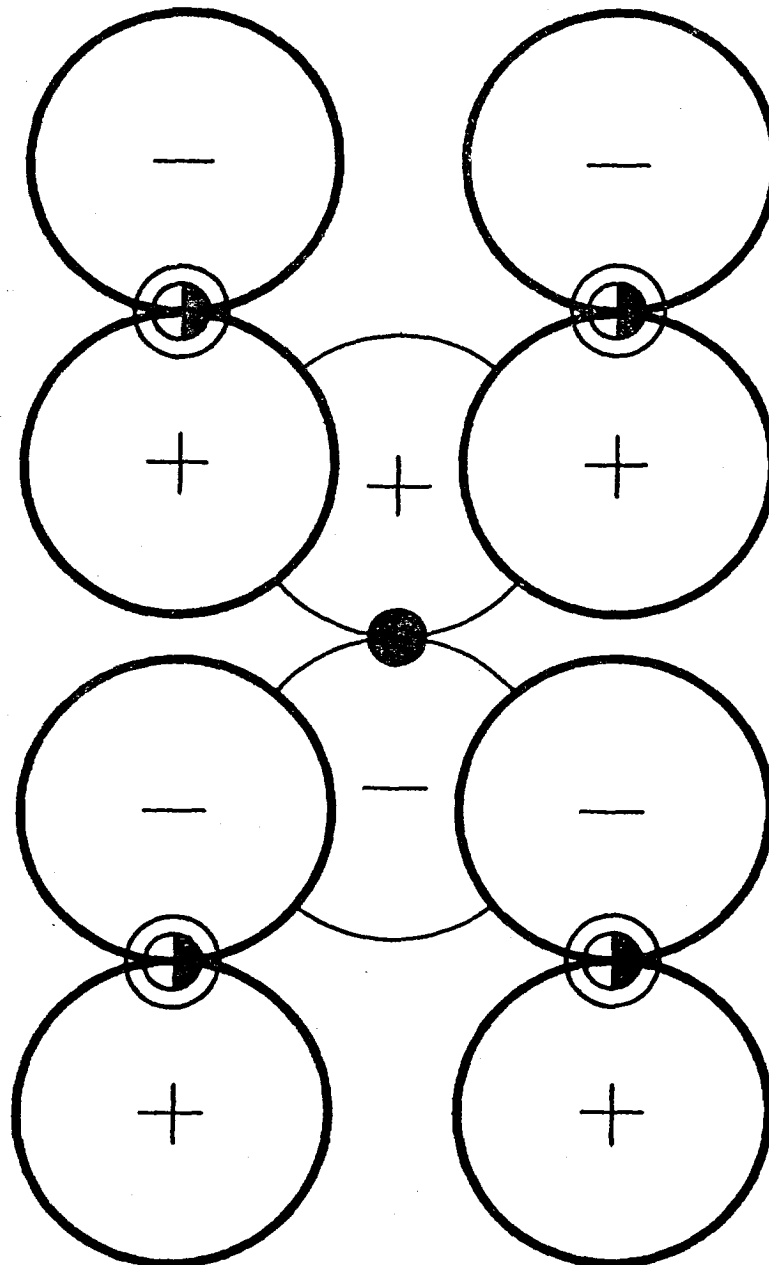
Figure 1. - Overlaps among orbital-pairs.

FOUR ATOMS ABOVE

FOUR ATOMS BELOW

ONE ATOM AT THE CENTER

Figure 2. - The body-centered cubic p band.
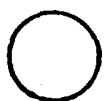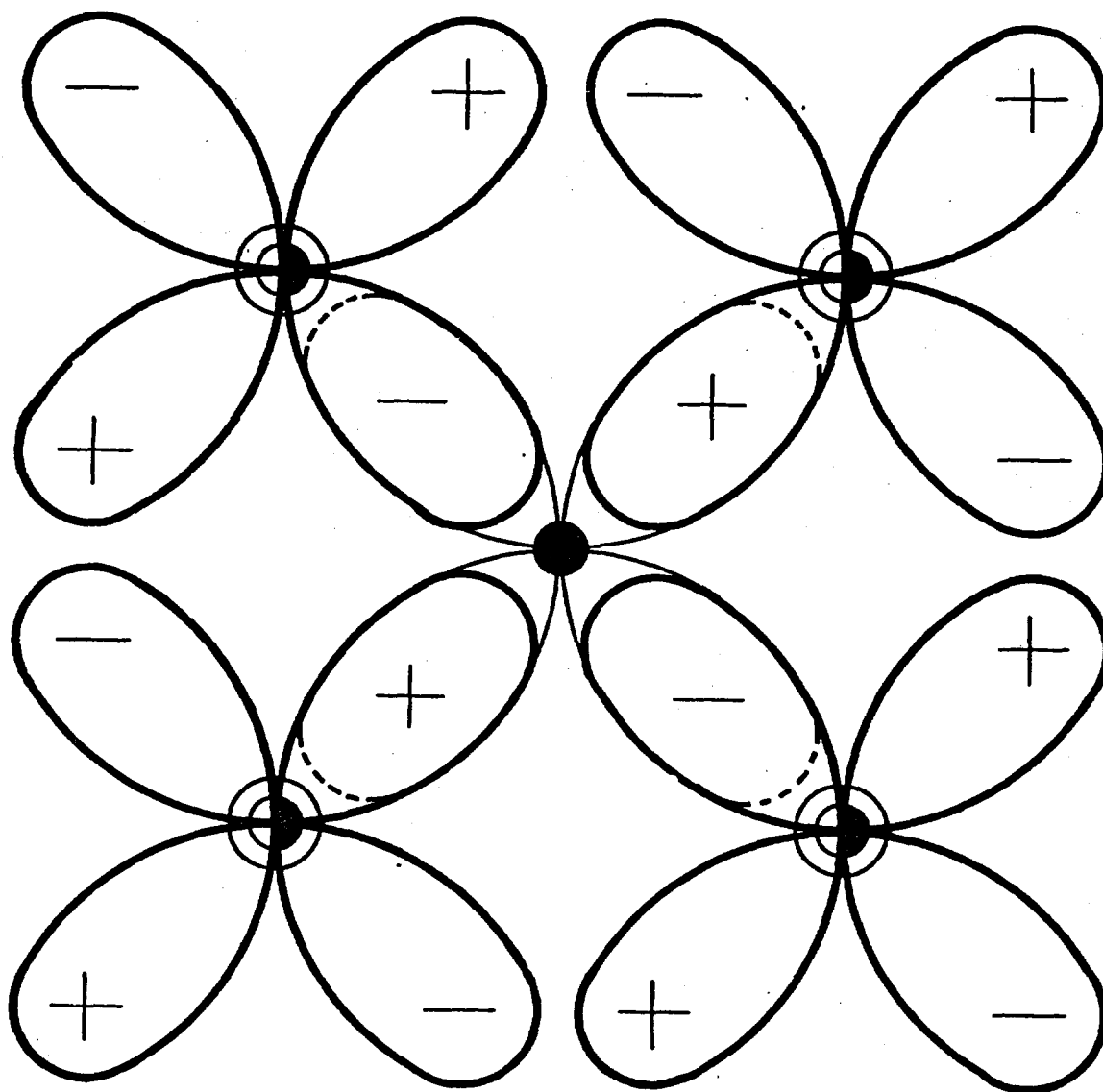
FOUR ATOMS ABOVE
FOUR ATOMS BELOW
ONE ATOM AT THE CENTER

Figure 3. - The body-centered cubic dε band.
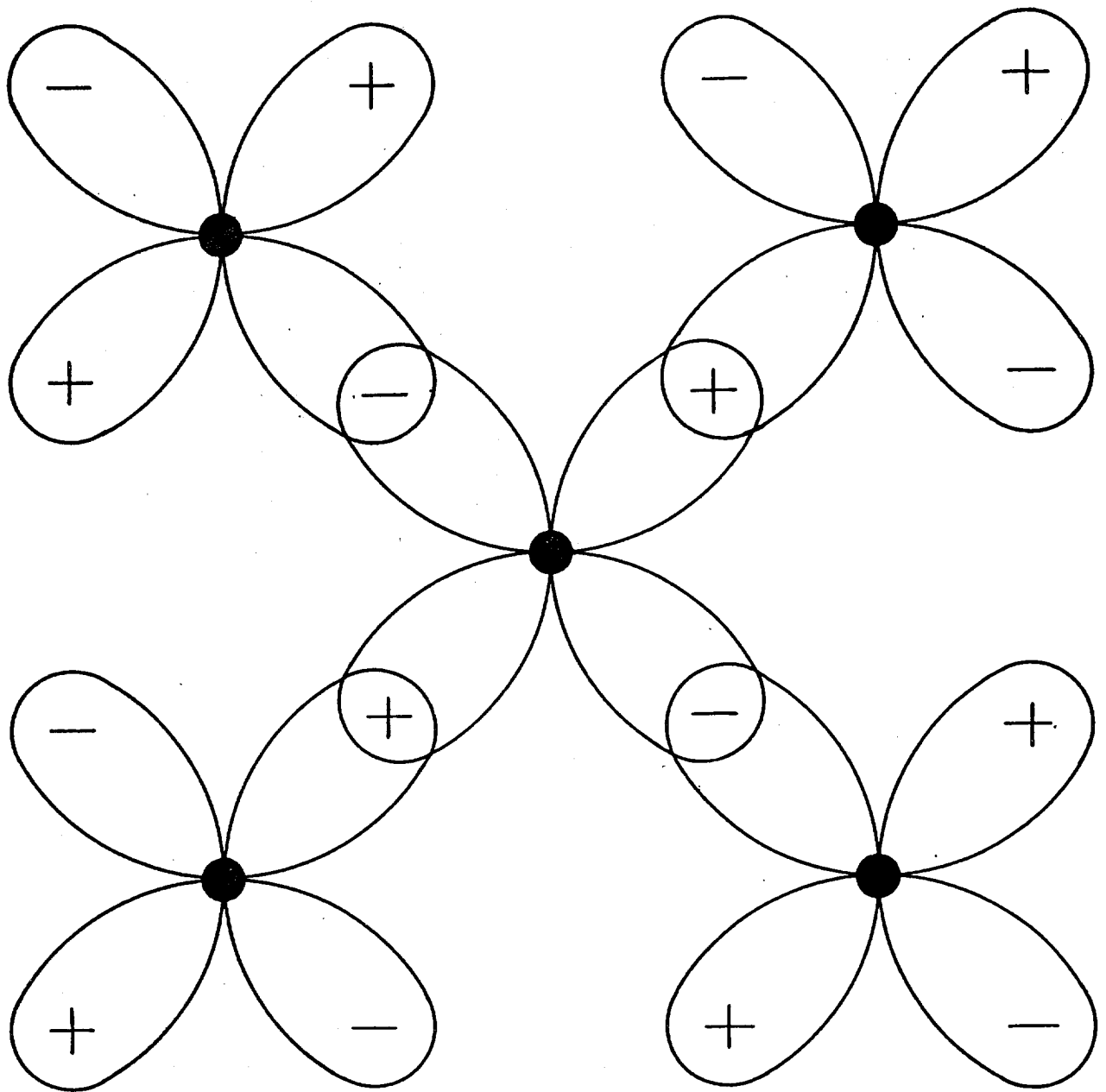
● FIVE ATOMS IN PLANE

Figure 4. - The cubic close-packed dε band.
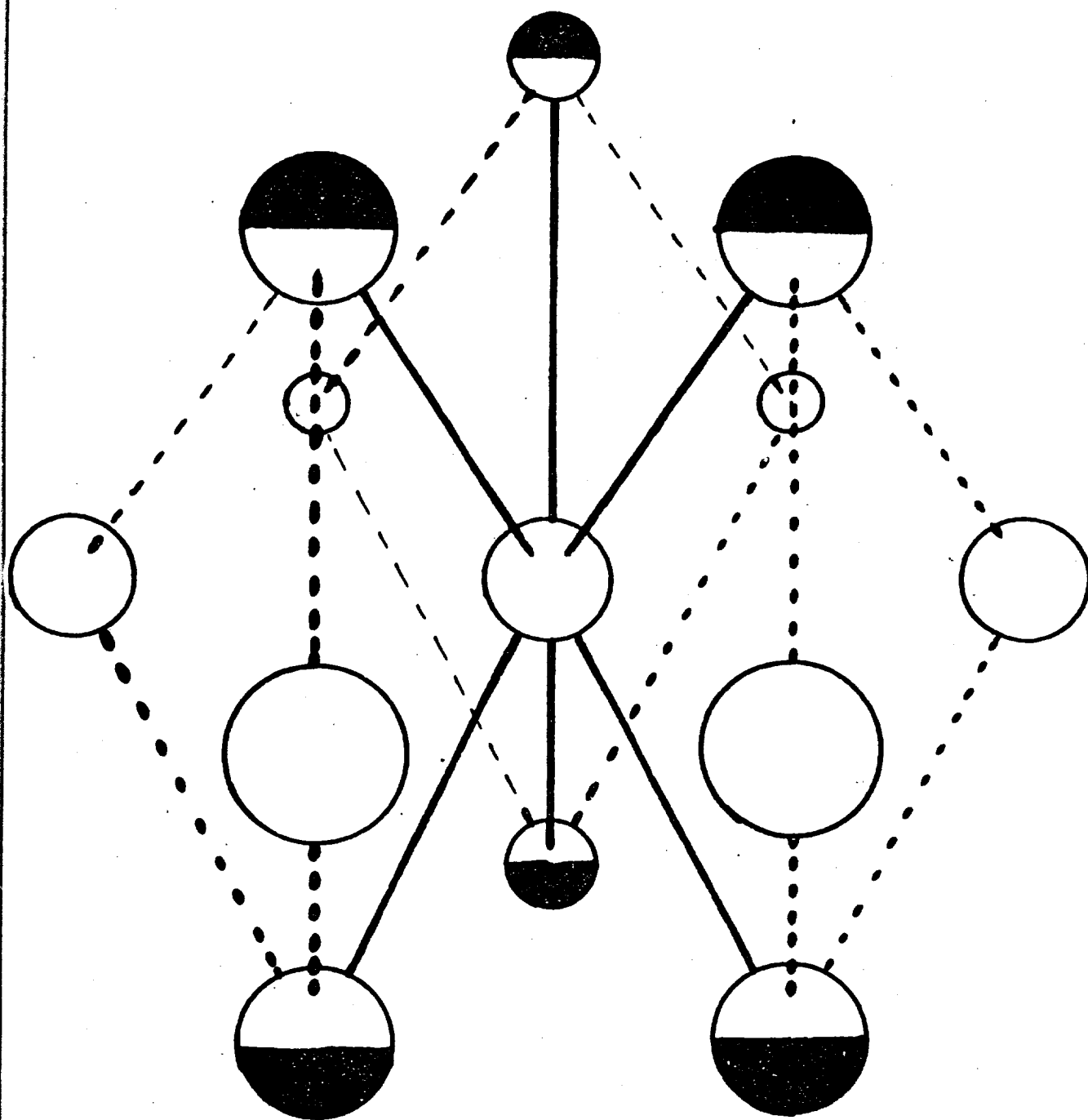
Figure 5. - The hexagonal close-packed hybrid band (sd^4p or d^5p).

XY PLANE

● Z,0 ◐ Z,1 ○ Z,-1
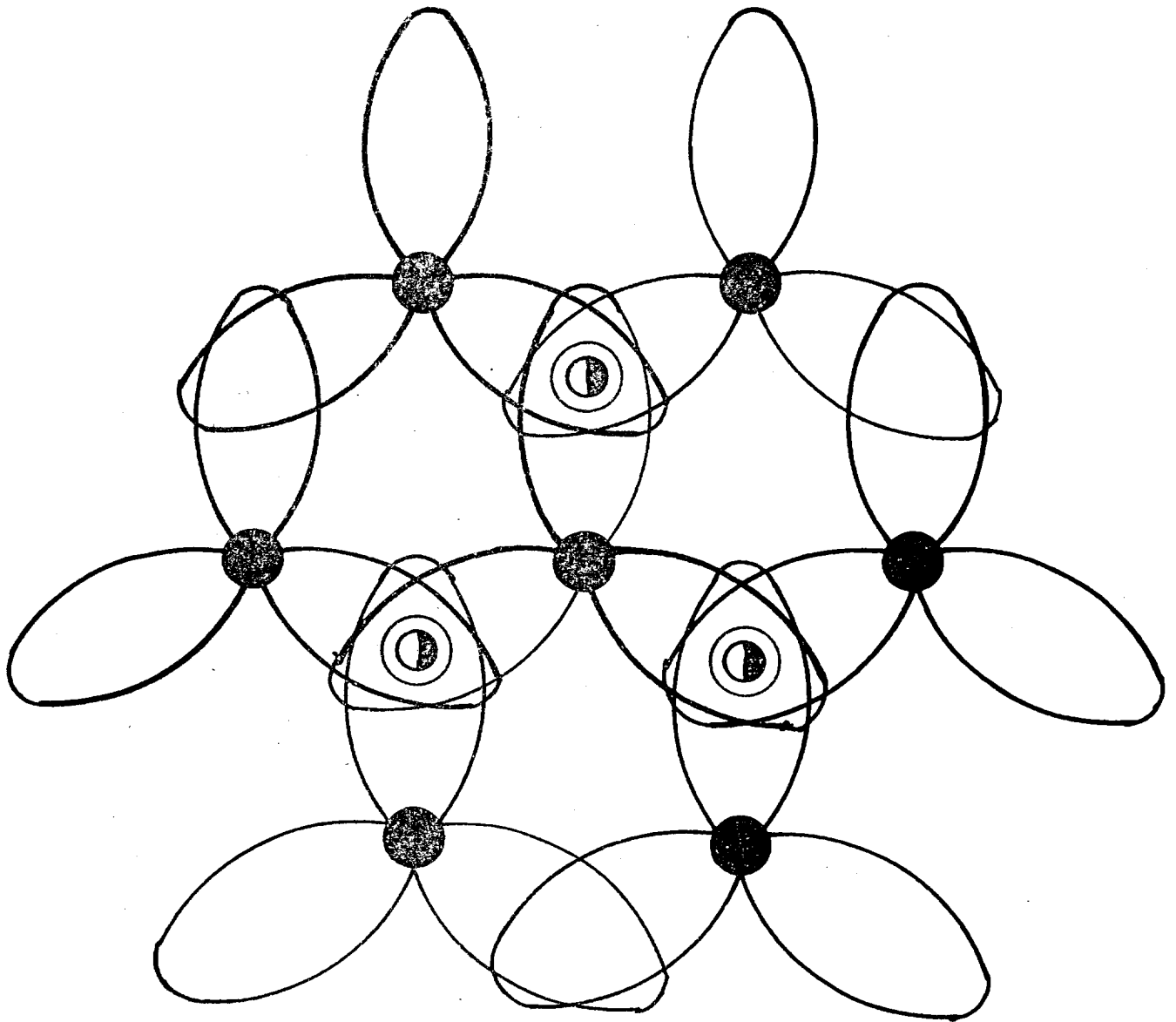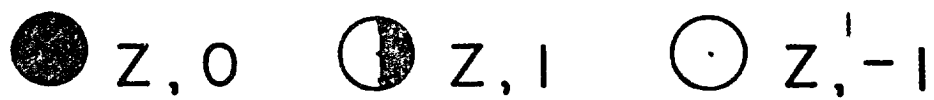
Figure 6. – The distorted hexagonal close-packed sp^2 band.
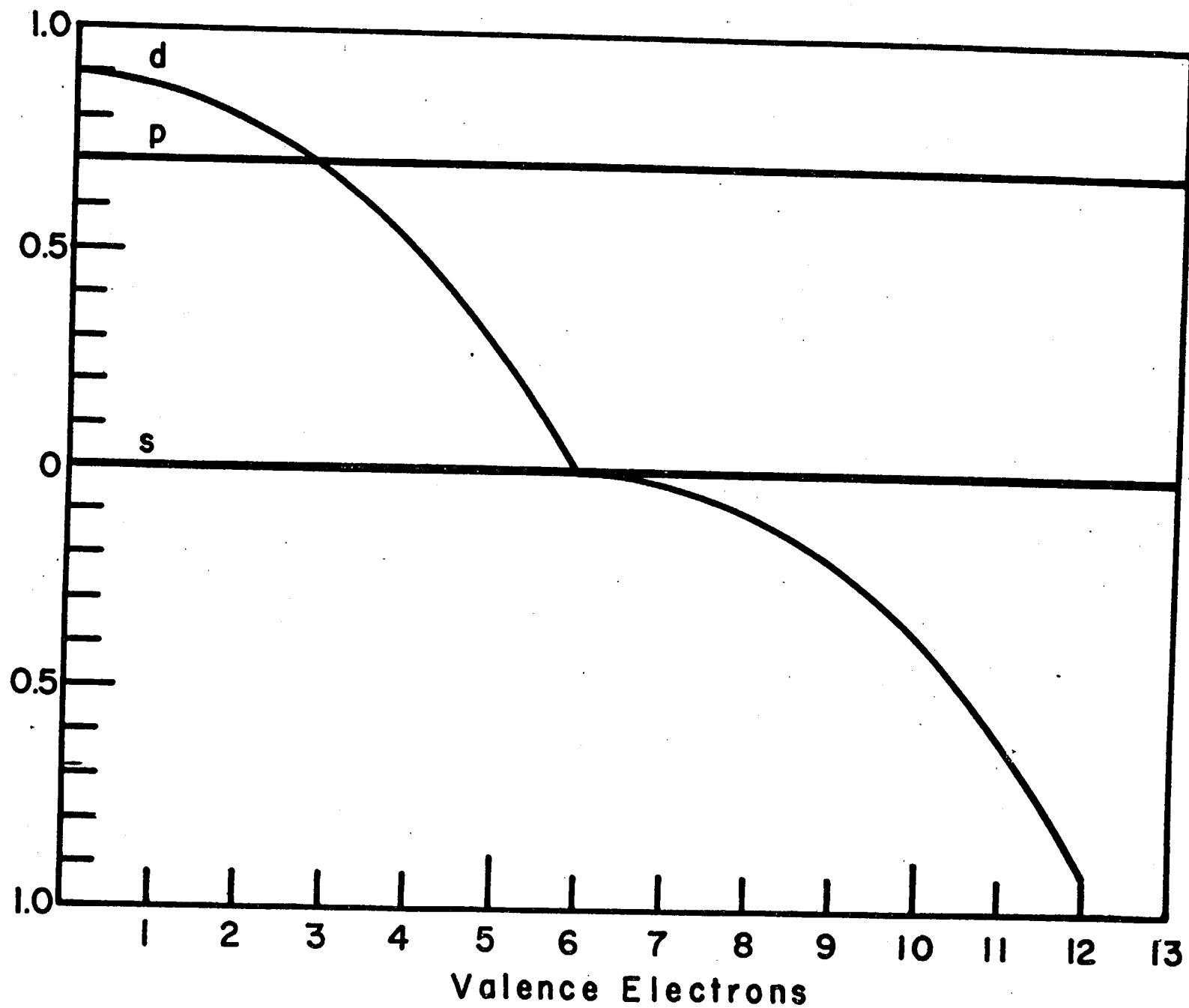
Figure 7. - Atomic orbital energy levels.
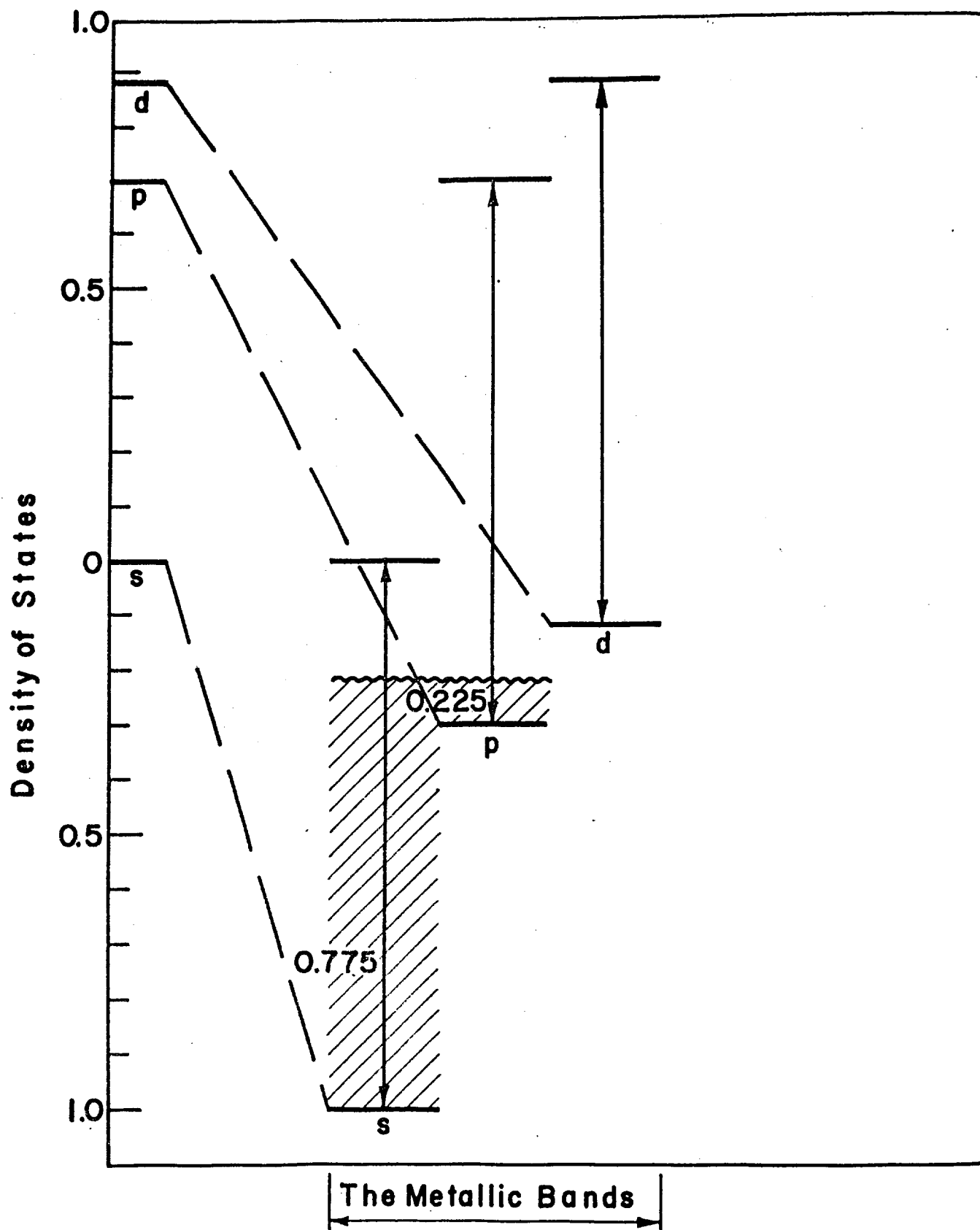
Figure 8. – Electron population chart for 1-electron atoms.
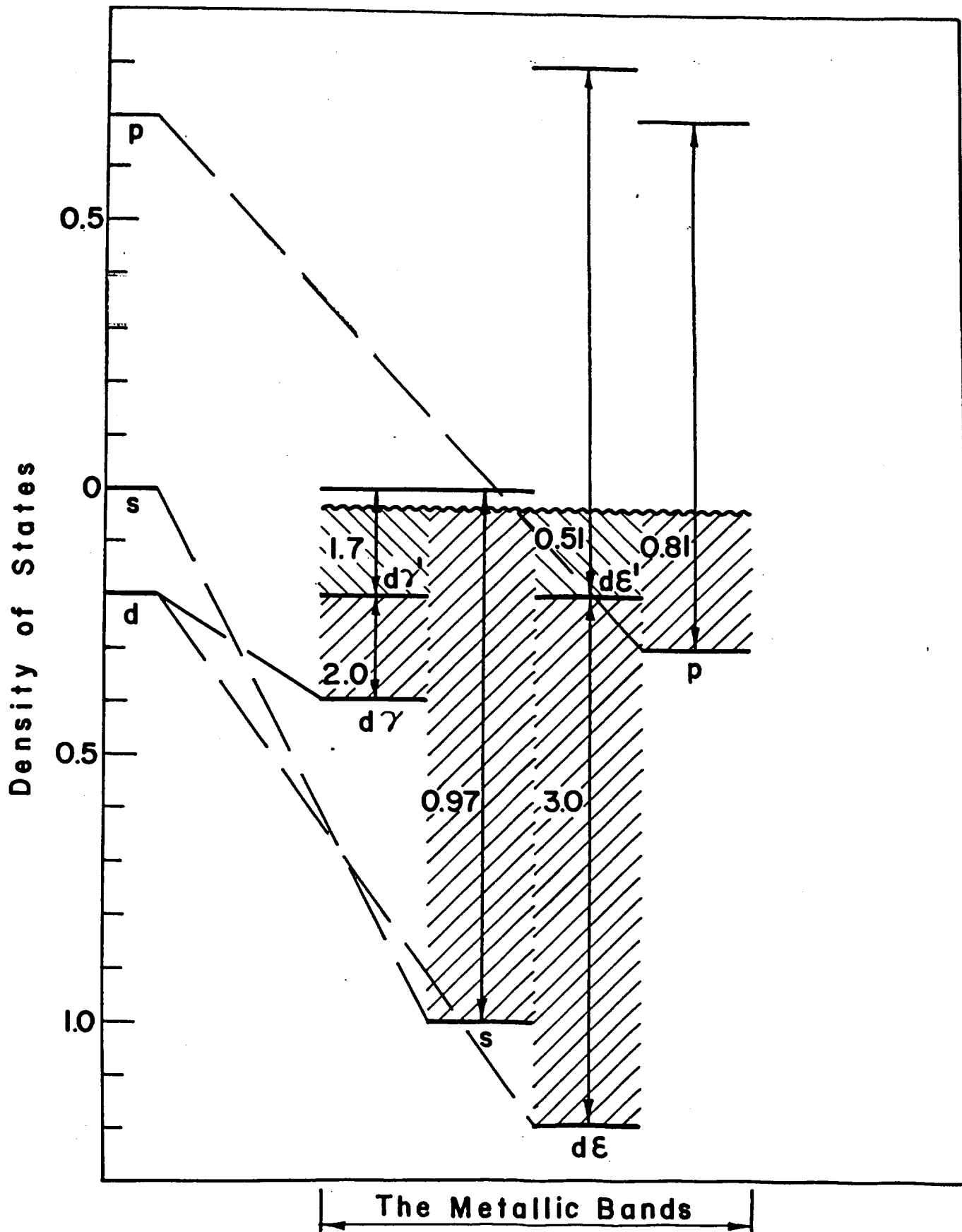
Figure 9. - Electron population chart for 9-electron atoms.
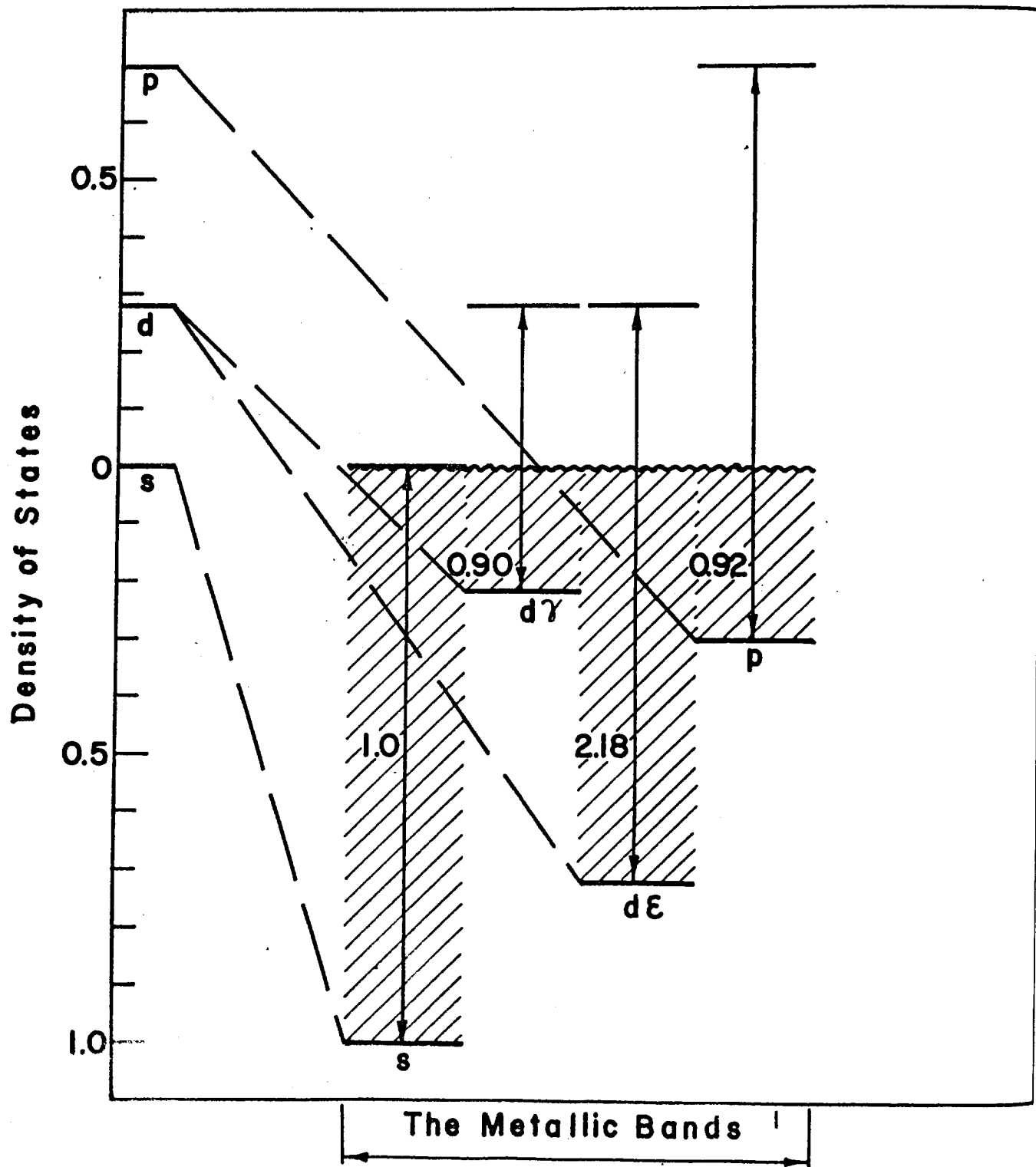
Figure 10. - Electron population chart for 5-electron atoms.
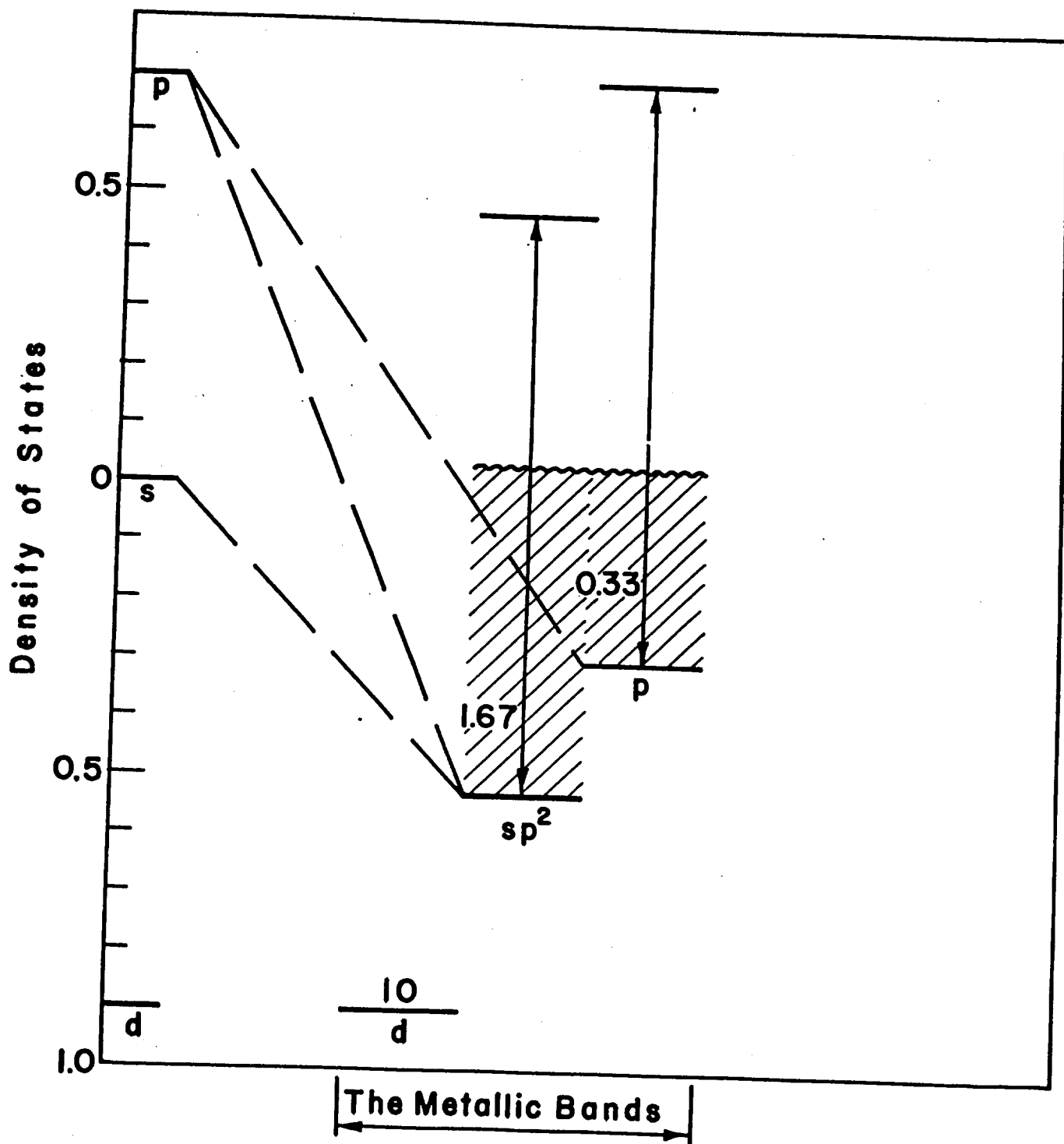
Figure 11. - Electron population chart for 12-electron atoms.

PART II - PHYSICAL PROPERTIES OF THE TRANSITION METALS

INTRODUCTION

The overall picture of the metallic bond, as it appears from the orbital constructions and electron populations for the transition metals, is of atoms held together by multiple, mostly weak, mostly directed forces. In the bcc metals, for example, every atom is bonded to each nearest neighbor seven times through orbital overlaps (with additional bonding to next nearest neighbors). Six of the overlaps (three d and three p) have a directive property. The interlobar binding energy in each of these numerous contacts is, however, not large. As an estimate, taking 50 kcal as the energy of a localized covalent bond, something like 4 kcal appears as the order of the binding energy for two overlapping lobes in bcc $d\varepsilon$, when the electron density is 0.66. Degeneracy simplifies these rather complex interactions into three band systems (with a fourth one for next-nearest neighbors), each of which has cubic symmetry. The band systems then combine to provide the lattice energy of the body-centered cubic element. In this picture, three rather different groups of properties can be distinguished, depending on whether the properties of the nuclei in the lattice, or the properties of the lattice as a whole, or the properties of the electrons in the bands, are being considered. A few words will be said about each of these groups of properties in what follows.

NON-ELASTIC PROPERTIES

The forces resisting non-elastic nuclear displacements depend on the nature of the overlap functions and on the electron

populations associated with the overlaps. Consequently, properties like ductility, hardness and malleability will have different dependencies on the several bands within a band system, and will vary from lattice to lattice. In the bcc system, for example, a particular rolling motion is possible in the p_x band, in which atoms in one layer move around an atom in another layer with no change in overlap and hence no resistance to the motion. In bcc dε , any movement of one atom with respect to another is hindered by an overlap change. The s band, on the other hand, offers no resistance to any rolling motion. In the bcc system, therefore, the bands become less ductile in the order bcc s, bcc p, bcc d ε . Counting electron densities and the nature of the restraints imposed by the bands in s^1 and s^2d^3 elements, it at once becomes evident that, although both are body-centered cubic, the first (potassium) is to be quite soft and the latter (vanadium) hard, relative to each other.

There is also what seems to be a significant difference between the cubic and hexagonal systems with respect to non-elastic displacements. The directed localized bands in the 6-, 7- and 8-electron atoms imply a greater measure of hardness than the delocalized bands in the cubic (bcc and ccp) systems. Not only is the number of net bonding electrons at its highest, but the proportion of them in the hard bands is also highest in the 6-, 7- and 8-electron atoms. The distorted hexagonal close-packed layer is intermediate in this regard, with the more malleable delocalized restraints between the layers, and less malleable more localized restraints in the layers.

A consideration of the lattice defects in these systems is also possible. A vacancy can be seen in the bcc bands, for example, in terms of a new set of overlaps between next nearest neighbors; s-s, p-p π , d-d δ in the s, p and dϵ bands, respectively. The vacancy contracts, as a result of these compressive forces, and adjacent nuclei are displaced from their normal lattice positions. The vacancy may be thermally stable or unstable, depending on whether the lattice energy is thereby increased or decreased. Seen in this way, the vacancy has little effect on properties of state like melting points and heats of phase change, but retains its important mechanistic role in kinetic phenomena like diffusion, ductility, etc.

THE BINDING ENERGY

Turning to the total binding energy, which is the sum of the contributions of the several bands, variations that can be described in the three following statements are shown. Correlations are to be sought between binding energy and such lattice properties as elastic constants, melting and boiling points, heats of phase change, etc. To be specific, comparisons will be made with melting points.

1. From the number of net bonding electrons (Table 1), the binding energy, and hence the melting points, should have a maximum value at the 7-electron atom, except in the first long period, where Mn and Fe are required to be anomalous.

2. From the consideration that the d band gives more stability to the bcc than to the ccp lattice, it is to be expected that the binding energies and melting points of the bcc transition elements should exceed those of other transition elements with the same number of bonding electrons (i.e. $s^2d^2 > s^2d^8$; $s^2d^3 > s^2d^7$;

$s^2d^4 > s^2d^6$). The melting-point variations in Table 1 conform with this statement.

3. From the conclusion that the contribution of the d band increases with the principal quantum number, the binding energies and melting points are expected to increase going down each sub-group.

These simple statements are, in general, borne out in the melting-point variations (Table 2), except that the maximum seems to occur at the 6- rather than the 7-electron atom, and that more than one bonding d electron must be present for the third statement to be correct.

TABLE 2

The Melting Points of the Transition Elements (°C)

Valence	3	4	5	6	7	6	5	4	3	2
First Period	Sc 1200	Ti 1800	V 1750	Cr 1800	(Mn) 1260	(Fe) 1535	Co 1480	Ni 1452	Cu 1083	Zn 469
Second Period	Y 1490	Zr 1900	Cb 2500	Mo 2620	Te	Ru 2450	Rh 1966	Pd 1550	Ag 960	Cd 320
Third Period	La 826	Hf 2200	Ta 2996	W 3370	Re 3167	Os 2700	Ir 2440	Pt 1773	Au 1063	Hg -39

PROPERTIES OF THE BANDS

The third group of properties, related to the presence of the electrons in the bands, includes electrical conductivity, para-magnetism, and ferromagnetism.

1. Electrical Conductivity

A first requirement for electrical conductivity is that single electrons be able to move from atom to atom throughout the crystal. This is possible in each delocalized band (i.e. bcc s, bcc p, bcc dε, etc.), for in them each atomic orbital overlaps

other atomic orbitals, that overlap others, etc. Moreover, each of

the four metallic lattices has at least one delocalized band.

In any one delocalized band, as all atomic orbitals are

the same, an electron can move from atom to atom without a change in

energy. Indeed, the energy levels within the band refer to the lattice

as the confining element of volume. In this situation, resistance can

only be associated with the restraints that are needed to transform

the free random movements of the electrons into a unidirectional

flow within a band. In a simple model, two processes are involved.

First, an electron concentration gradient must be set up within the

band. This is analogous to an ionization process (it will involve,

presumably, some states just higher than the ground states) and will

therefore principally reflect electron-nuclei interactions. Secondly,

the flow of electrons induced by the concentration gradient may be

dissipated into random motions by collisions between electrons in the

band. Thus the component of resistance derived from electron-electron

interactions will vary with the electron density in the delocalized

metallic orbitals. As the ionization potential and the electron density

are different in the delocalized d, s and p bands, the conductivities

should also be different. The resistance of graphite is about 1000

micro-ohm/cm. If this is taken as the order of resistance to be

expected in a conducting band that has an electron density of one and

a semi-metallic ionization potential, it can be used to roughly measure

the contribution of the d ε , and perhaps the s bands, to the

conductivity of the transition elements. The argument compares the p

orbitals of carbon with the d orbitals of a transition metal. The

resistance of such a metal is of the order of 10 micro-ohm/cm. The

p band, therefore, appears to provide about 90% of the observed
conductivity of the metal, and s and d bands the remainder. The result
implies a temperature dependence for resistance. Assuming that electrons
are excited from s and d into p levels at higher temperatures, the
change in electron density makes the p band less, and the d band more,
conductive than before. If the p band makes much the greater
contribution, as is indicated, the total conductivity decreases as the
temperature is raised.

2. Paramagnetism

Paramagnetism is another property that may be associated
with the presence of single electrons in metallic molecular orbitals.
As a measured quantity, paramagnetic susceptibility is a complex
factor, since it is the difference between the diamagnetism of the
electron-pairs and the paramagnetism of the unpaired electrons. In
thinking of the equilibrium, $2 e^1 \rightleftarrows e^2$, in a particular band, it is
to be remembered that electron-pairs from other bands also contribute
to real susceptibility values. The paramagnetic contribution in
itself, however, can be related only to the number of unpaired
electrons (per atom) in the metal.

Two situations can occur. Either the atomic orbitals have
combined with one another to form bands, in which case the electrons
have become bonding entities; or, if the orbitals do not touch (or
if they repel each other), the electrons are non-bonding and remain localized
in the atomic orbitals. In the first case, the unpaired electrons,
if any, are to be found in the delocalized bands, their number and
concentration dependent on the equilibrium between single and paired
electrons in that band. This situation leads to paramagnetism, while

the second can produce the property of ferromagnetism and will be considered later.

In the bcc s, p and dε bands, one orbital overlaps eight others. Electron-pairing can therefore occur within the volume of a unit cell if each orbital has, on the average, 0.22 electron. If the electron density is much less than 0.22, each electron pair sets up zones of positive and negative charge, spread over finite portions of the band. (If the electron density is 0.1, for example, the electrons from 20 orbitals must concentrate in, at most, 9 orbitals, to form an electron pair. The negative charge will be spread over the nine, and the positive charge over the eleven orbitals.) This is equivalent to an ionization process and will oppose electron-pairing, though only at rather low electron densities. It is therefore suggested that though electron-pairing may be relatively complete for electron densities substantially greater than 0.22, it is incomplete at this and lower values. As the electron density counts both single and paired electrons, the maximum concentration of single electrons in any band will be considerably less than 0.22. If, for example, the number of single and of paired electrons is about the same, when the electron density is 0.22 the concentration of single electrons will be about 0.07 electron per orbital. Typical values for real metals (in which diamagnetism has diminished the paramagnetism) are of the order of 0.01 electron per atom. The electron densities almost always exceed 0.6 electron per orbital in the s, d and hybrid bands, but are always less than 0.4 in the p bands (Table 1). The conclusion is that the observed paramagnetism of these metals is largely, though not necessarily altogether, a property of the under-populated p band.

The importance of $s^1 \rightarrow p^1$ in lithium and sodium is difficult to assess. Upper and lower limits, however, can be put on the transition. An even distribution of the electron among the four states provides the upper limit, 0.25 electron per orbital. This is close to the electron-pairing value, 0.22, for orbitals in bcc. Here all bands could show some paramagnetism. A lower limit comes from assigning the paramagnetic susceptibility entirely to the p band. Taking $e^1 \sim e^2$, and allowing as much again for the diamagnetic susceptibility, about 0.06 electron per atom appears in the p orbitals; that is, among a hundred lithium atoms, at least six $s^1 \rightarrow p^1$ transitions have occurred.

3. Ferromagnetism

α-iron has a body-centered cubic lattice despite the fact that it is an 8-electron atom with an $s^2 d^6$ ground state. In an external magnetic field, α-iron can be magnetized to a saturation value of 2.2 electron spin moments per atom, a fact generally accepted as an indication of unpaired electrons in the (n-1)d orbitals. Part of the ferromagnetic property is the phenomenon of hysteresis, and the behaviour at the Curie point. The problem, then, is to explain the structure of the metal and the complex ferromagnetic property, through orbital constructions and electron populations. The expectation is that the solution will be unique to α-iron. The argument follows.

It was concluded in Part I that an 8-electron transition metal should have an hcp lattice based on the sd^4p band. This makes use of four d orbitals in the principal band. Failing this, three d orbitals could be placed in ccp dε , leading to a cubic close-packed lattice. On no account, because of the antibonding population in the

important next nearest neighbor band, bcc dγ', could a body-centered cubic lattice be justified if it were to be determined by the three diagonal d orbitals. α-Fe, nevertheless, has a body-centered cubic lattice. This can only mean, if the general argument is still to be valid, that the two axial, rather than the three diagonal, orbitals form the principal bands in this case. That is, the dγ level is to lie below the dϵ in α-Fe. This is the unique aspect of the α-Fe structure.

Taking the bcc p and s bands as before, a particular arrangement of the d orbitals exists that places the axial orbitals (d_{z^2}, $d_{x^2-y^2}$) in good bonding positions, and the diagonal orbitals (d_{xy}, d_{xz}, d_{yz}) in what amounts to a non-bonding construction. For this, the d sub-shell is to be turned from its position in bcc dϵ , bcc dγ by 45° about the X and 45° about the Y axis. The lattice is unchanged but the orbitals touch differently. In the new arrangement, each axial orbital overlaps four nearest neighbors. (In the d_{z^2} band, a central orbital overlaps four others at an interlobar distance of 0.58. In the $d_{x^2-y^2}$ band, the central orbital overlaps orbitals from the four remaining nearest neighbors in the 1x8 coordination unit.) The axial orbitals together constitute what will be called the α-Fe dγ band. The diagonal orbitals have orientations that are incompatible with simple or substantial overlaps. When orbitals touch, contacts between lobes of similar and dissimilar sign are both to be considered. That is, the α-Fe dϵ band approximates a non-bonding band, and will be so taken. When the electron populations of this band system are calculated, with the methods and assumptions of Part I, the values shown in Table 3 (page 51) are obtained. The

ferromagnetic property is to be associated with these orbital
constructions and electron populations.

With a population of 4.5 (Table 3), the non-bonding dε
band has, on the average, 1.5 single electrons and 1.5 electron pairs
on each atom. The single electrons have magnetic moments associated
with their spins, whereas the electron pairs are diamagnetic. The spin
magnetic moment, the distribution of the spins in the dε band, and
spin interactions with an external field, provide the bases from which
the ferromagnetic property is to be discussed. There are three points
to be made:

First, a magnetic coupling occurs between single electrons
in like orbitals (e.g. d_{xy},d_{xy},etc) if the spins of the electrons
are parallel. This gives rise, as more spins are so aligned, to an
internal magnetic field that keeps the spins so oriented in what will
be called the magnetic dε band.

Secondly, as both the spin property and the charge pattern
in an orbital may have one orientation or its opposite, three ways of
arranging adjacent diagonal orbitals exist. These are: $+d_{xy}$, $+d_{xy}$;
$+d_{xy}$, $-d_{xy}$; and $-d_{xy}$, $-d_{xy}$. The +,- pattern, in which adjacent spins
have opposite signs, is a bonding arrangement with respect to both
spin pairing and the sign on the overlap function, which is positive
(as in a d-dπ arrangement, Figure 1, Part I). The +,+ and -,- patterns,
in each of which parallel spins are in juxtaposition, are on the other
hand non-bonding, both with respect to the spin alignment and with
respect to the negative sign on the overlap function. That is,
magnetically coupled parallel spins are to be associated with an
interorbital repulsive term, if there is an overlap volume. (This

repulsion is not to be confused with the antibonding property of an antibonding band. Here the spins are paired, not parallel.) In effect, therefore, the single electrons are localized on single orbitals in the magnetic band, though the magnetic coupling is 'delocalized' and extends over the band. In the absence of an external field, therefore, the magnetic d band consists of three regions. The first (+,+) and the third (-,-) localize electrons on the orbitals and set up internal fields with opposite signs. The third (+,-) is non-magnetic, and corresponds to the boundary region between (+,+) and (-,-)[*].

In the third point, it is to be seen that the property of spin alignment with a field splits the $d\varepsilon$ level into magnetic and anti-magnetic states. In $d\varepsilon$, the single electrons are in the magnetic, the electron pairs in the anti-magnetic band.

It is now possible to follow the changes that occur when α-iron is placed in an external field. As the (+,+) and (-,-) regions have exactly equal probability there will be no net moment before a field has been applied, no matter what the probability of the bonding (+,-) to the magnetic (+,+), (-,-) regions[**], or the distribution of the electron pairs. When a small external field is applied, either

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[*]As the bonding contribution from the α-Fe $d\varepsilon$ band is that of the (+,-) region, it is evident that the energy of this reaction must be of the order of, or less than, the energy of magnetic coupling in (+,+) or (-,-) if a ferromagnetic property is to appear. That is, the bonding interaction must be of a very low order, but it is not necessary that it be precisely zero.

[**]This picture corresponds closely with the domain theory of Weiss (10), particularly if the probability of the (+,-) regions is so small that they occur only as boundary lines between the (+,+) and (-,-) regions. The latter are then the domains within the crystal whose opposed magnetic moments make the crystal non-magnetic.

the (+,+) or the (-,-) region is favored. As the favored region

grows, there appears in the specimen a net magnetic moment that

reaches a maximum (which will be shown to be spurious) when all

are in parallel alignment. This maximum amounts to 1.5 spin moments

per atom, as the electron pairs cannot contribute.

The electron pairs are diamagnetic and oppose the field.

Moreover, they decrease the coupling in the magnetic band by increasing

the distance between electrons with parallel spins, and by decreasing

the number of spin states in the band. That is, the electron pairs

have a negative reaction to the external field and tend to be ejected

by it. The $d\varepsilon$ level splits into magnetic and anti-magnetic states, with

an energy separation that depends on the strength of the external field.

The anti-magnetic levels are excited not only with respect to the

magnetic states, but also with respect to the bonding bands $d\gamma$, s and

p. These energy levels do not vary in the external field (apart from

the small (0.01 e) paramagnetic interaction to be expected in the

conductivity bands). As a consequence of the field dependence excitation,

electrons move from the anti-magnetic into the bonding bands under the

influence of an external field. The movement of electrons simultaneously

increases the density of spins in the magnetic band; that is, the magnetic

moment continues to increase as the external field is strengthened.

It is not possible in a simple way to compare directly the

field dependent excitation in the anti-magnetic band with the field

independent levels in the bonding bands. An upper limit to the

migration of electrons into the bonding bands can be set, however, by

that electron density which if exceeded would cause a phase transformation

in the specimen. From the rule of thumb (Part I), the maximum electron

density for a stable bcc p band is 0.4 electron per orbital. Taking the energy level for this electron density as defining the upper level to which electrons can be excited in all bands, the electron populations in the band system of α-iron in an external field of maximum strength can be calculated and are shown in Table 3. With 3.3 electrons in dε (2.7 e^1 in the magnetic and 0.3 e^2 in the anti-magnetic band), a magnetic moment of 2.7 is to be associated with an external field of maximum strength.

TABLE 3

Electron Populations in α-Iron as a Function of the External Field

Bands in α-Iron	Electron Populations	
	No External Field	Maximum External Field
p	0.8	1.2
s	0.9	1.0
dγ	2.0	2.0
dγ'		0.4
s'		0.1
dε	4.5	3.3
Net bonding electrons	3.5	3.7

A further comment is perhaps worthwhile in respect to the interaction between α-iron and the external field. A small increase (0.2, Table 3) in net bonding electrons occurs as the external field moves 1.2 electrons from the anti-magnetic to the bonding bands. The net change is small because the additional levels occupied in the conduction band (the p band) are largely counterbalanced by a new antibonding population in dγ'. (The changes in s and s' bands exactly counterbalance each other.) It would therefore seem correct

to conclude that the external field has increased the binding energy of the specimen, though by less than 6%. A conductivity dependence on the external field is also indicated, as the p band population increases by 0.6 electron per atom.

There are two points still to be made. First of all, when the external field is removed, electrons may be expected to return to the dε band from the molecular orbitals, for the ground state condition once more obtains. At the same time, the magnetic moment of the specimen falls, from the saturation value of 2.7 to the permanent value, 1.5. The decrease is a spontaneous demagnetization that follows the removal of the external field. Thus, two processes, that can be distinguished from each other, contribute to the property of ferromagnetism. One is an alignment of spins within the non-bonding dε band; the other is a flow of electrons between the magnetic and bonding bands. The first, once established, can be maintained without an external field (the internal field does it); it can therefore be identified with the permanent magnetic moment. The second process, the flow of electrons among the orbitals, is spontaneously reversible once the field is removed. These two processes together reproduce the form of the hysteresis curve for α-iron, though the numerical agreement is rather poor (1.2 and 2.2 against 1.5 and 2.7 for the permanent and the maximum moments, respectively). (The disagreement is of the order of the increase in the number of net bonding electrons, 0.2 per atom, so the latter need not be real.)

The next concern is the Curie point, the temperature at which the property of ferromagnetism disappears. In the model for α-iron this can most easily be imagined as the temperature at which the 3d

sub-shells of the atoms can begin free rotations. The Curie point can then be roughly estimated, from the melting point, by assuming that the binding energies in the bands are proportional to their electron populations. Only the restraints in the α-Fe dγ band need be overcome to permit free rotations of the inner core within the bcc s, bcc p bands. With 2 bonding electrons in the former, and 1.5 in the latter, the Curie point becomes 2/3.5 of the melting point, or 760°C. The correct value is 770°C. The possibility that a phase change accompanies or follows the Curie transition depends on whether or not the diagonal orbitals, at the higher temperatures, can make appreciable contributions to the binding energy. As evident possibility, in the model, is a transition to a cubic close-packed lattice, in which the diagonal orbitals use ccp dε. Though this does provide the lattice of non-magnetic γ-iron, the transition to it does not occur at the Curie point.

PART III – CHEMICAL REACTIONS IN THE TRANSITION ELEMENTS

INTRODUCTION

The band systems of the transition elements place all $(n-1)d$, ns, and np orbitals. To follow a chemical reaction, account is to be taken not only of the valence state of the transition element but also of the valence state of the element with which reaction is occurring. There are three distinguishable (but not entirely independent) variations that can occur:

1. In the kinds of orbitals used

   e.g. d,s,p vs d,s,p; d,s,p vs s,p; etc.

2. In the electron content of the orbitals

   e.g. s^2d^3 vs s^2d^2; s^2d^3 vs s^2d^9; s^2d^3 vs s^2p^2; etc.

3. In the relative sizes of the orbitals

   e.g. $3d, 4s, 4p$ vs $2s, 2p$; $3d, 4s, 4p$ vs $4s, 4p$; etc.

It is perhaps to be noted that these variations include such derivative properties as electronegativity, valence, space packing, degeneracy, etc. Each variation can have specific effects on the course of reaction and on the final product.

In compound formation, the same problem is encountered as in the construction of the band systems for the transition elements, namely the discovery of the orbital constructions and electron populations for the correct molecular orbitals. In the compounds there is, however, an increase in the variety of orbital interactions to be considered. These are to be interpreted, if possible, both in respect to the course a reaction might take, and in respect to the dependence that physical properties and structure may show on the composition of the compound. In what follows (where Zn, Cd and Hg will not be counted

as transition elements), compound formation will be discussed under these headings:

1. Alloys (s^2d^a vs s^2d^a)

2. Intermetallic compounds (s^2d^a vs s^2p^b)

3. Interstitial compounds (($n-1$)d, ns, np vs 2s, 2p)

ALLOYS

A rather simple situation exists in principle when both elements have an active d shell. Then, as the band systems of each are known and are in each case derived from the same atomic orbitals (d,s,p), each lattice can tolerate a considerable exchange of atoms within its own band system. Two factors, however, make the band system of the alloy deviate from that of the pure metal. In the first place, as the two elements have, in general, different numbers of valence electrons, the electron population in the alloy changes with composition. Secondly, as like orbitals on unlike atoms (e.g. $d_{xy}A, d_{xy}B$) will be partly distinguishable (either because of a different charge on the nucleus or because of a difference in the principal quantum number), electron distributions and orbital interactions will be somewhat different in an alloy than in a pure metal. These two factors (electron populations and orbital size factor) will be discussed separately and then brought together to give a composition diagram for these binary alloys.

In considering the electron populations in an alloy as a function of composition, it is evident that a particular problem is the variation in the d level across a period. This means that the d bands in the alloy are to be made from two kinds of orbitals that are otherwise similar but have different non-bonding levels

(e.g. $d_{xy}A$, $d_{xy}B$). Though this points up a characteristic difference between a metal and an alloy, it unfortunately makes the calculation of electron populations more difficult. If it be assumed that a single non-bonding level exists in the alloy, at the composition average level of the two, the difficulty is overcome. The simplification, which is tantamount to assuming that $d_{xy}A$ and $d_{xy}B$ are interchangeable despite their differences, may be permissible inasmuch as aspects related to the differences can be taken up separately. Band systems, electron populations and a lattice can be obtained at once for this 'alloy as an element'. A 30-70 alloy from 5- and 11-electron atoms respectively is, for example, given the band system, the electron population and the lattice of a 9.2-electron atom. The valence electron number of the alloy changes continuously with composition and, of course, also differs when the end-members change. Three classes of binary alloys are thereby obtained, as follows:

1. An alloy from two elements that have the same band system shows no lattice change over the composition range between pure end members (Figure 12a).

2. An alloy from a cubic (bcc $d\varepsilon$ or ccp $d\varepsilon$) and a hcp (d^5p or sd^4p) metal, has one lattice change in its composition range (Figure 12b). The transformation occurs at compositions that give an average of 6.5 or 8 valence electrons per atom, for bcc and ccp respectively. (For example, an s^2d^3, s^2d^6 alloy changes from bcc to hcp at a 50-50 composition. The value, 6.5, is taken because the 6-electron atom is still dimorphic, bcc and hcp.)

3. Two cubic metals (one body-centered from bcc d ϵ , the other close-packed from ccp d ϵ) will give an alloy with three different lattices over the composition range between pure end-members (Figure 12c). The transformations occur at compositions that give an average of 6.5 and 8 valence electrons per atom. As an example, an alloy from $s^2 d^3$ and $s^2 d^9$ elements changes lattice at 75 and 50 mole percent $s^2 d^3$, from bcc to hcp to ccp respectively.

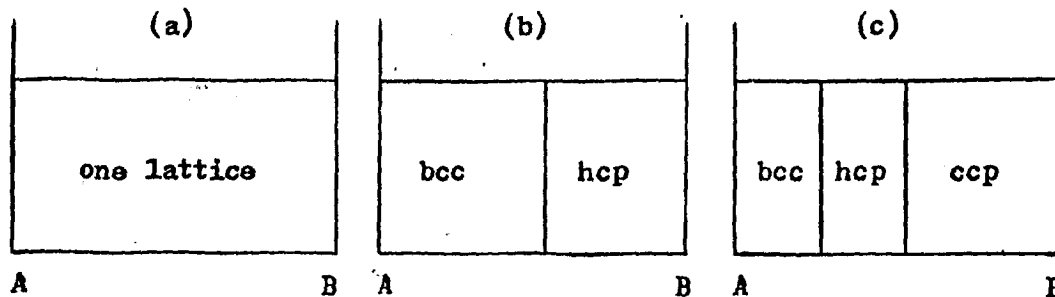| (a)	(b)	(c)
one lattice	bcc hcp	bcc hcp ccp
A B	A B	A B

Figure 12. - Lattice-composition diagrams.

Something like 350 binary alloys (Zn, Cd and Hg are excluded) are to be placed in the three catagories. About 85 are found in the first, 110 in the second, and 80 in the third. The rest are uncertain, either from uncertainties in the band system (e.g. the 3-electron atoms), or because of dimorphism in the band systems (e.g. the 6-electron atoms). For each alloy, the electron populations and attendant physical properties change in a prescribed way as the composition changes between pure end-members.

Two conditions are to be attached to these general conclusions. First, and rather unfortunately, alloys in which Fe or Mn are major components are to be considered as special cases. Secondly, the conclusions are valid only insofar as the differences in like orbitals (e.g. $d_{xy}A$, $d_{xy}B$) are in fact reconciled by the assumed composition average orbital in the alloy. That this identity will not in fact be

perfect can be seen at once in the electronegativity property.
Inasmuch as electronegativity can, on electrostatic grounds, be
related to the closeness with which an electron cloud is associated
with the nucleus, an uneven distribution of electrons is implied
whenever like orbitals of dissimilar size interact. This can have
consequences both with respect to electron populations in the alloys
(particularly when antibonding and non-bonding levels are to be
occupied) and as regards an enhanced stability for certain compositions.
Evidence for the importance of such a contribution can come from the
occurrence of order-disorder transitions in alloys.

In practice, if an alloy (say bcc) is made from the melt,
no lattice exists during alloy formation. Quick quenching may freeze
the atoms in a random arrangement in a lattice. The s,d and p bands
will then consist of a random set of A-B, B-B, and A-A overlaps. In
general, a greater binding energy will be provided either by the
overlaps between like atoms (A-A, B-B) or by those between unlike
atoms (A-B); that is, the quick-quenching process will likely freeze
the alloy in a metastable state. Two disorder-order phenomena can be
visualized. In the first case, the bond between the like atoms is
the stronger. An annealing process produces an alloy that is a mixture
of minute crystals of A and B. The crystals are to be small, for
the ordering process can only occur in volume elements through which
the atoms can diffuse. The crystal forms of A and B need not be the
same. Hence the alloy need not have a large scale unit of order.
In the second case, when A-B overlaps make the better contribution a
disorder-order process can occur in an infinitely large crystal, if
the composition is correct. A 50-50 alloy has A-B overlaps exclusively

in the bcc s,p and dϵ bands of a body-centered cubic lattice when the structural units are alternately AB_8 and BA_8. The overall picture is that of layers of pure B alternating with layers of pure A. The atoms in a layer do not touch each other (except in dγ, the next nearest neighbor band). Hence, in an annealing process, a disordered A_1B_1 alloy, no matter how large the crystal, can achieve the ordered structure by an exchange of atoms between adjacent loosely packed layers.

Ordered structures richer in A are possible, but do not have the same margin of stability as the 1:1. For example, the next ordered structure in bcc has the formula A_3B. All B atoms are surrounded as in BA_8, but these units alternate with AA_8. The overall structure has layers in which A and B atoms alternate, sandwiched between layers of pure A.

It is evident that to achieve an ordered structure the annealing temperature must be high enough to give the atoms the thermal energy that enables them to escape from the A-A and B-B bonds, but not from the stronger A-B overlaps. That is, the disorder-order transition can only go to completion below the melting point of the alloy; whereas, for it to begin, the temperature must be high enough to provide the activation energy for the exchange reaction.

At issue in these order-disorder transitions are what might be called the orbital size factors, that is, those properties that can be directly or indirectly related to the differences in otherwise similar orbitals. There are, in general, two kinds of differences to be considered. First of all, like orbitals may differ in themselves, as in $3d_{xy}$ vs $5d_{xy}$; or, secondly, interactions between like orbitals may be influenced by differences in other orbitals, as in dϵ ^{3} (with dγ^0) vs dϵ ^{3} (with dγ ^{4}).

In the model, two elements with the same number of valence electrons have the same band systems and electron populations. The orbitals differ only in the principal quantum number. Unless this difference becomes critical (as would be indicated, for example, in the radius ratios), simple miscibility is implied for the binary alloys. As the alloy and the pure metals are in all respects similar, only a small free energy change, and this largely in the entropy term, can be associated with the reaction (i.e. there is no change in the number of net bonding electrons). It is therefore possible that immiscibility can occur, though miscibility is the general expectation. As the A–B interactions (in the overlap and exchange integrals) will in general be close to, but either more or less than, the (A–A,B–B), a small disadvantage in A–B may change the sign of $\triangle F$. As there is no alternate lattice, what might be called an accidental immiscibility is produced.

Immiscibility is, however, still less likely when the transition elements have different numbers of valence electrons. The differences then are such that if the normal band system is denied the alloy, a compound with an anomalous band system will still be established. In brief, a heat of reaction term has become important. This can be seen in an alloy made from 5- and 9-electron metals (e.g. A s^2d^3 and B s^2d^7).

When two elements with d^3 and d^7 sub-shells combine, the band systems of either (bcc $d\varepsilon$, $d\gamma$ and ccp $d\varepsilon$, $d\gamma$) are open to the other. Substitution in each end-member lattice is permissible. The elements differ, however, in that the d^7 levels are the lower lying (Figure 7, in Part I) and the d^3 bands have the smaller populations

(Table 1). It is to be noticed that those are opposing trends, for while electrons move from d^3 to d^7 because of the difference in the non-bonding energy levels, they move from d^7 to d^3 to increase the number of net bonding electrons. It is to be concluded at once, therefore, that the magnitude of the charge in any +,- charge pattern implied for the alloy is to be less than would otherwise be expected. This can be seen in the cubic phases. The $d\epsilon$ band provides the greater binding energy in both bcc and ccp, while $d\gamma$ has the more important antibonding levels. In bcc, d^7 acts to increase the number of bonding electrons in the underpopulated bcc $d\epsilon$ band, and keeps a non-bonding population in $d\gamma$. In ccp, d^3 increases the number of net bonding electrons in ccp $d\epsilon$ (by decreasing the antibonding population) and ccp $d\gamma$ remains non-bonding. In both cases, the charge transfer occurs largely in the $d\epsilon$ band, electrons moving from d^7 to d^3. The transfer in $d\gamma$, which is from d^3 to d^7, is in this instance small, as the $d\gamma$ levels in d^7 are fully occupied. Since the population in the bcc $d\epsilon$ band is 2.18 (Table 1), the maximum charge that can appear at any lattice point is -0.82. (The charge pattern in the s and p bands may assist or oppose the d band pattern.)

The hcp lattice is the simple prediction for intermediate compositions in alloys from 5- and 9-electron elements, because the net bonding population thereby attains its maximum value ($\sim$ 7 electrons per atom compared with 5 for the cubic end-members). To achieve this, however, five d orbitals (one in d^5p; four in d^4sp) must become bonding orbitals on every atom. A transfer of 2 or 1 electrons from d^7 to d^3 is therefore necessary to set up the hcp band system.

$$d^3 + d^7 = 2 d^5$$
$$d^3 + d^7 = d^4 + d^6$$

If this is not possible (that is, if the antibonding levels on d^7 lie too far below the bonding levels on d^3), the hcp band system will presumably not form. Extensions of the cubic modes (or unpredicted new band systems) may still be able to take advantage of the increase in net bonding electrons that reaction produces. That is, compounds are still expected in the intermediate zones, although the band systems and lattices may not accord with the simple predictions. When one end-member is hcp and the other cubic, the tendency will be to shorten the hcp and extend the cubic phase in the alloy.

Combining the arguments based on orbital differences, it may be concluded that deviations arising from differences in like orbitals (assuming miscibility) will have their most pronounced effect at compositions that can give A-B overlaps exclusively in the alloy bands. 1:1 compositions are best for this in bcc, hcp, and ccp. Second-best compositions are 1:3 in bcc and ccp. Consequently, the composition diagrams, in addition to showing lattice changes at prescribed compositions, may be expected to have some anomalous property at 1:1 compositions in all lattices, with minor anomalies at 1:3 in cubics. When differences in other orbitals are also to be counted, as in d^3 vs d^7 sub-shells, an additional uncertainty is introduced into the intermediate composition regions. The differences in A and B are at their greatest in the case of the third lattice-composition diagram, Figure 12c. In this instance, an hcp lattice was predicted for the sensitive intermediate region and is therefore the prediction most likely to lack generality.

Finally, on combining the effects arising from the similarities and from the differences in the orbitals, the overall conclusion is that three kinds of composition diagrams are to be expected, each of which has an anomalous property near the 1:1 region. The anomaly may vary from the appearance of an ordered lattice to the appearance of an anomalous lattice, at that composition.

INTERMETALLIC COMPOUNDS

In considering the reactions between s^2d^a (element A) and s^2p^b (element D), the range of compounds that includes intermetallics, interstitials and salts is implied. The A and D orbitals are not, in general, interchangeable, so that structure-composition diagrams showing continuous compound formation over the composition range, as in the transition metal alloys, can not, in general, be expected. Rather, the problem becomes the discovery of the orbital constructions and electron populations that are correct for the A-B compounds as specific cases. These are already well known for the salts, but are less well known in intermediate cases. The latter will be considered here.

When s^2d^a (element A) and s^2p^b (element B) have some bonding properties in common (as, for example, in Cu, $s^2d^9p^o$, and Zn, s^2p^o, where the s and p orbitals are similar), a compound with orbital constructions and electron populations that differ from either end-member is still to be expected, as the band systems of the transitional and non-transitional elements are incompatible with each other. There is, however, the additional possibility that a limited substitution in the end-member systems can also take place. In what follows, brief statements about these substitution compounds will be made, and the

formation of a compound which differs from either end-member will
then be discussed in some detail.

An element, D, that has its $(n-1)d$ sub-shell completed has
ns, np valence orbitals remaining to it. The substitution of atoms
of D for A in the lattice of the latter can lead to p_a-p_d and s_a-s_d
but not to d_a-d_d overlaps. That is, the substitution can be accommodated
by the s and p but not by the d bands of the transition metal. The
ground state of the element D can be s^2p^0, s^2p^1, etc. Compared with
A (s^2d^a), D has as many or more p electrons and no d orbitals. Hence,
each substitution of an atom of D for A increases, at the same time,
the electron density in the p band, and withdraws electrons and orbitals
from the d bands. The result is a relatively rapid reduction in the
binding energy of the latter (as both electrons and overlaps are
removed), partly balanced at first by an increased stability in the
p band. Such properties as hardness and melting point are largely
determined in the A elements by the d bands, while electrical
resistances and paramagnetism depend on the electron density in the
p band. The changes in the d and p bands are such that the resistance
and the diamagnetic susceptibility of the alloy increase, and its
melting point falls, as the concentration of D and A rises.

It is to be noted that two partly independent band systems
are being built up in the single lattice as substitution continues.
Because there is no mechanism to transfer electrons from the non-
transition element (s^2p^b) into the d bands of the transition element,
the s and p bands (made up from A-D overlaps) are independent of the
d bands (made up from A-A overlaps) so far as the D element is
concerned. As the d band is progressively destroyed by the substitution,

it is only in the p band that a lattice retention property can be found as the element D is added. Even in the cubic p band, however, no further stability is to be gained once the electron density exceeds 0.4 electron per orbital (from the rule of thumb, Part I). Accordingly, what will be called p band solubilities can be calculated from composition average electron densities in the p band. The calculated electron densities in the cubic p band of the pure metals are close to 0.33. The p orbital population in the D atoms can be taken from their valence states $(s^2p^b \rightarrow s^1p^{b+1})$. (That is, the s band population in the alloy, as in the transition metal, is to remain at 1 electron per orbital. The assumption implied here, that antibonding s levels are not occupied until the p orbital population exceeds 0.4, is a restatement of the rule of thumb.) From these figures, the saturation solubility of the p band occurs at the compositions shown in the following tabulation for s^2p^0, s^2p^1 and s^2p^2 elements in s^2d^a:

Element B	Electrons per p orbital in D	Composition of saturated p band (0.4 electron /orbit)
$s^2p^0 \rightarrow s^1p^1$	0.33	miscible
$s^2p^1 \rightarrow s^1p^2$	0.66	0.78 A, 0.22 D
$s^2p^2 \rightarrow s^1p^3$	1.0	0.89 A, 0.11 D

In the case of the s^2p^0 element, where the p band shows miscibility over the composition range between end-members, the inclusion of the contributions from other bands leads to the conclusion that atom solubilities are, in general, less than p band solubilities. Taking $Zn(s^2p^0)$ and $Cu(s^2d^9)$ as a specific example, it is evidently impossible for the ccp band system (Table 1) to persist up to the zinc end-member, as is implied by the p band miscibility, for the

distorted hcp system of the s^2p^0 atoms (Table 1) will eventually become dominant as substitution progresses. Judging from the number of net bonding electrons (3 and 2 for Cu and Zn respectively), the transition from the ccp to the distorted hcp band systems would occur at 40-60 Cu-Zn. This composition is, however, already richer in Zn than is the composition (50-50 Cu-Zn) in which an ordered lattice eliminates the Cu d band as a bonding entity in ccp. Moreover, the solubility of Cu in Zn (which will cost one bonding d electron per atom of Cu dissolved) will certainly be less than the solubility of Zn in Cu. It is therefore to be expected that the solubility of Zn in Cu will be somewhat less than in a 50-50 Cu-Zn alloy. The further addition of zinc may then produce a Cu-Zn compound whose lattice and band system differs from that of either end-member, if this can provide a binding energy for the Cu d electron.

The qualitative conclusion to be drawn from the p band solubilities is that the s^2p^b elements become less soluble in the transition metals as the electron content of the p orbitals increases. The instability in the d band, which is always introduced by such a substitution, lowers the net binding energy of the alloy relative to the pure end-members. As a consequence, real solubilities will always be less than p band solubilities. The instability in the d band varies with the mole fraction of the s^2p^b element, and with the d band population of the transition element. The p band solubilities therefore become unapproachable upper limits to atom solubilities, which in turn vary with respect to the d orbital (in s^2d^a) and p orbital (in s^2p^b) populations in A and D respectively.

The differences between the cubic (bcc $d\xi$ and ccp $d\xi$) and hexagonal systems (d^5p and sd^4p) is significant to these solubility reactions. As the hcp p band is only doubly degenerate, it cannot accommodate all three p orbitals of the s^2p^b elements. If the electron transfer is nonetheless complete, the hcp p band will more quickly become saturated. Not only is the p band solubility less in hcp than in cubic systems; the d band instability (which in hcp is to be associated with the trigonal hybrids) is greater in hcp than in cubics. This follows, for on the one hand the population of bonding electrons is at its maximum in the trigonal hybrids, and on the other, the substitutions (of s^2p^b for s^2d^a) eliminate all of the bonding property of each localized bond that is broken. In the delocalized cubic d bands, fractional portions of the bonding interaction provided by each orbital disappear with each substitution. Because the p band solubility is less, and the d band instability greater, in hcp than in the cubic systems, the s^2p^b elements will be less soluble in hcp (the 6-, 7- and 8-electron elements) than in the cubic transition elements. Since, moreover, the s band, which is a solubilizing factor in the cubic elements, is absent (i.e. it is absorbed in the hybrid configuration) in hcp, the difference in solubility will be marked. This can be seen from a comparison of the numbers of bonding electrons that facilitate and oppose solubility in the two cases. In the cubic systems, the s and p band populations assist, and the net bonding populations in the d bands oppose, solubility. In hcp, it is the p band population against that of the trigonal hybrids. From the values of the ratios of 'soluble' to 'insoluble' electron populations,

it may be concluded that solubilities in the

	bcc (5-electron atom)	ccp (10-electron)	hcp (8-electron)
$\dfrac{\text{s and p}}{\text{d}}$	$\dfrac{1.92}{3.08} = 0.64$	$\dfrac{1.88}{1.88} = 1.0$	$\dfrac{0.50}{6.0} = 0.08$

cubic are of the order of 10 times as great as in hcp.

It is perhaps evident that these conclusions provide a basis for devising semi-quantitative diagrams for the solubilities of the thirty-six s^2p^b elements in the thirty transition elements (s^2d^a). Solubility diagrams for approximately a thousand binary pairs are indicated. Semi-quantitative predictions with respect to certain physical properties are attendant on the composition diagrams. It is beforehand to attempt a detailed comparison with established data, but the general trend agrees with what is known. The conclusions can have reference only to those compositions which precede the appearance of new orbital combinations. Distinctive orbital combinations that establish new compounds in new regions of the composition diagram come from a more detailed study of the elementary identities of $A(s^2d^a)$ and $D(s^2p^b)$. These are more specific interactions and can, of course, condition the general conclusions in the specific cases.

INTERSTITIAL COMPOUNDS

Compounds of a distinctive type are formed when two elements, A (s^2d^a) and D (s^2p^b), bond to each other through d-p overlaps. In describing these compounds, the orbital construction of the dp band system will be given first. Then will be considered the conditions to be satisfied for such a band system to be established in AD compounds, and the properties of those compounds. Finally, some attention will be given to the effect, on the compound, of changes in the d and p sub-shell populations in A and D respectively.

The construction of the dp band follows from the orientations and positions the atoms must have to permit maximum bonding between the d and p orbitals. The symmetry and shape of the p and d orbitals determine that the reaction of the p orbitals be with the three diagonal d orbitals (the $d\epsilon$ level). The overlaps are of the $dp\pi$ type (Figure 13). When all orbitals are so arranged, a triply degenerate dp band is constructed, coextensive with the lattive. The structural features of the dp band are octahedral DA_6 and AD_6 units (Figure 14) that are spatially so arranged as to reproduce the rock-salt lattice. The formula of the compound is A_1D_1.

Two conditions are to be satisfied if the compound is to form from A (s^2d^a) and D (s^2p^b) elements. It is, first of all, necessary that d-p (rather than p-p) overlaps be assured. It is also necessary that bands be established that contain the orbitals not included in the dp system. The first condition is satisfied if the p orbitals of D (s^2p^b) are smaller than either the p or d of A (s^2d^a), as can be seen in Figure 15. Then the p-p overlaps vanish at bond lengths for which the d-p overlaps are still substantial. (It has been separately shown (6) that d-p overlaps have their largest values when d is larger than p.) Associating the size of the orbitals with the principal quantum number, it is to be concluded that only those elements that have 2p valence orbitals will, in general, be able to form these compounds, and then only with the transition elements (where 4s 3d 4p valence orbitals, etc., are used).

The condition that bands for the remaining valence orbitals be also found is still to be established. The repeating units in the dp band system are the two patterns in Figure 14. It is evident from

the figure that, although the diagonal d orbitals touch each other, their substantial overlaps do not produce a net overlap function, for + and - overlaps are equal in magnitude and number. (The dp overlaps that do not have π-symmetry also cancel out.) The point is that the dp construction brings the metal atoms into contact with one another, and in so doing prescribes the orbital constructions of the remaining bands. The metallic atoms are closely packed in a cubic close-packed lattice. As a result, ccp s, p and dγ bands are established and all valence orbitals are counted. In the end, the non-metallic atoms (D, s^2p^b), firmly embedded in the dp band that establishes the structure, are also engulfed by metallic electrons (from the ccp s, p and dγ bands based on A, s^2d^a) with which they have no direct association.

To simulate a chemical reaction in which the compound A_1D_1 is made from the elements, D will be specified as $2s^22p^3$, i.e. the nitrogen atom, and A as $4s^23d^3$, which is vanadium. The metal has bcc s, p and d bands. For the reaction to begin, the dp overlaps must begin to be established. The metal atoms use the same orbitals (d_{xy},d_{xz},d_{yz}) in the dε band of the metal as in the dp band of the compound. The chemical reaction therefore begins in the (n-1)d sub-shell of the metal. The d orbitals must turn by $\pm 45^\circ$ as the dε band of the metal transforms into the dp band of the compound. For the reaction to go to completion, however, the metal atoms must also migrate, as the original body-centered lattice of the metal transforms to the ccp lattice for metal atom packing in the compound. That is, the chemical reaction is made up of distinguishable parts. The first step, a surface reaction requiring no activation in the metal, may

depend on the state of the gaseous component. The second step, however, depends mostly on the metal. The internal rotation that is required (of the n-1, within the n shell) must overcome the restraints the d orbitals provide in the metal. In A (s^2d^3), using the population data for the 5-electron atom, the d orbitals contribute the binding energy of 3.08 electrons per atom. If it is assumed that the whole atom has mobility and can rotate freely in the melt, it may be reasonable to conclude, from the numbers of electrons involved, that the internal rotations become possible, and the chemical reaction can therefore begin, at temperatures about 3.08/5 of the melting point. As vanadium (s^2d^3) has a melting point of 1750°C, vanadium nitride should begin to form at about 775°C. (The temperature is perhaps high enough to assure the presence of nitrogen atoms, or a suitably excited counterpart, in the gaseous feed.) To complete the reaction, all atoms must move from one position to another. Superficially, it is only necessary for the open metallic lattice to collapse into the closely packed lattice of the compound, as the reaction zone extends, since the volume of the compound is less than the volume of the metallic element alone. However, the directed forces in the metal still oppose the otherwise spontaneous migration. That is, the second step must overcome the restraints of the p, as well as of the d, orbitals. Taking account of the electrons in the p and d bands, and using the same assumptions as before, the reaction can go to completion at temperatures about 3.92/5 of the melting point. In the specific case of vanadium nitride, this is at 1313°C, still well below the melting point of vanadium itself.

The next consideration is the effect that changes in the electron populations may have on the interstitial compounds. Principal requirements for the compound were shown to be that a triply degenerate dp band be established, and that the element D have $2p$ valence orbitals (i.e. be a member of the first short period). The result of varying the s^2d^a element will be followed first.

dp, $d\gamma$, s and p bands can be specified in the compound, A_1D_1. The energy level of the dp band depends on the energy levels of the d and p atomic orbitals and on the binding energy of their interaction. As the p orbitals do not change in a series (say the nitrides), these orbitals will act to smooth out variations (though some still remain) in the dp band following changes in the atomic d orbital energy levels (Figure 7, Part I). In any case, the dp band will lie below the corresponding $d\varepsilon$ band (the difference in these energy levels is the source of the major part of the heat of reaction) and will therefore be more heavily populated and more deeply buried than a metallic band. The $d\gamma$ level in the compound is a weakly bonding band, like the bcc $d\gamma$ and ccp $d\gamma$. The $d\gamma$, the s and the p bands are independent of the nitrogen atoms. They will therefore be in much the same situation, relative to each other, as in a corresponding metal. In brief, the change from the metal is that dp is more stable and constant relative to $d\gamma$, s and p than would be $d\varepsilon$.

From the above considerations it is possible to summarize the electron populations of the interstitial compounds. The 4-, 5-, 6- and 7-electron elements (s^2d^2, s^2d^3, s^2d^4 and s^2d^5) will each have a full dp band (3 electrons per atom from A and from D) with additional populations, depending on the element, in the bonding levels of the

dγ, s and p bands. It is not possible to conclude, without a closer definition of band widths and levels, whether s^2d^1 will fill the dp band, or whether some population will also be found in s and p. At the 8- and 9-electron atom (s^2d^6 and s^2d^7), the band levels are such that the (antibonding) dγ' level becomes occupied.

8-electron atom: dp(3); dγ(2); dγ'(1); s(1); p(1).

9-electron atom: dp(3); dγ(2); dγ'(2); s(1); p(1).

This is equivalent to the presence of one (in the 8-electron atom) or two (in the 9-electron atom) unshared electron pairs in the axial orbitals. Both d_{z^2} and $d_{x^2-y^2}$ constitute inner core repulsions so directed as to specifically restrict dpπ-overlaps, as may be evident from the figures. The dp overlaps can still be retained in part if the interaction between the repulsion and the binding energy lowers the degeneracy of the diagonal d orbitals. This amounts to a promotion of electrons from dγ' to dp', with the antibonding population in the lattice localized on specific d orbitals. In brief, therefore, the A_1D_1 interstitial compounds can only be unambiguously associated with transition elements that have from 3 to 7 valence electrons. The argument implies that some opportunity for dp overlaps remains in the 8- and 9-electron elements, but the composition and the structure must be different, and the stability less, than in the A_1D_1.

The above arguments apply to nitrogen ($s^2p^1p^1p^1$) and to carbon ($s^1p^1p^1p^1$), with the difference that the carbon s orbital (s^1) is bonding and will therefore contribute to the s band, whereas the nitrogen s orbital (s^2) is non-bonding. Presumably the closed $2s^2$ sub-shell will make the inner core repulsions in the nitrides of the 8- and 9-electron elements more important than in the carbides.

Other members of the first short period, like boron ($s^1p^1p^1p^0$) and oxygen ($s^2p^2p^1p^1$), as they either under- or over-populate the dp band, would have to be considered as special cases.

Some physical properties of the compound appear directly from the model. First of all, as A_1D_1 retains a metallic p band, it should also possess the properties for which the band is principally responsible in the metal, namely metallic conductivity and paramagnetism. Secondly, since the atoms of D are located in lacunae in DA_6 octahedra, and the A atoms in the compound are more closely packed than in the metal (if it was bcc), A_1D_1 should have a smaller volume than A_1 alone. As a consequence of the increase in the number of the bonding electrons per unit volume (they approximately double), the compound should be harder, and have a higher melting point and a larger lattice energy, than the metal. Finally, as the stability of the compound is altogether a three-dimensional property, the compound cannot be presumed to persist beyond its melting point.
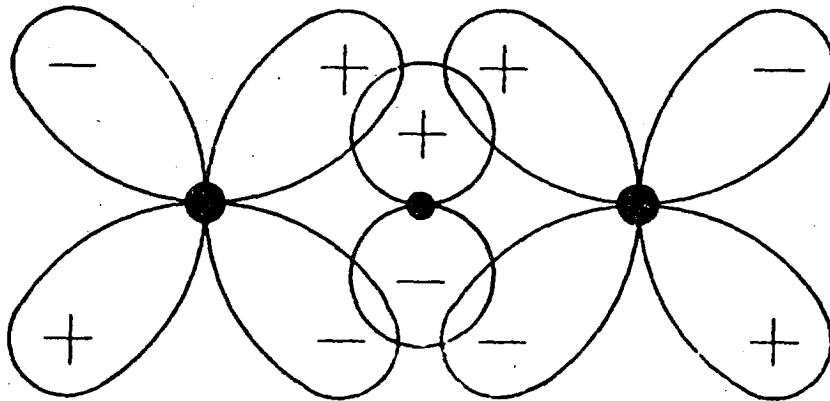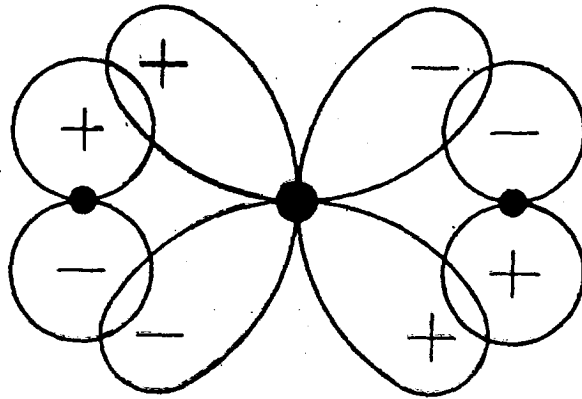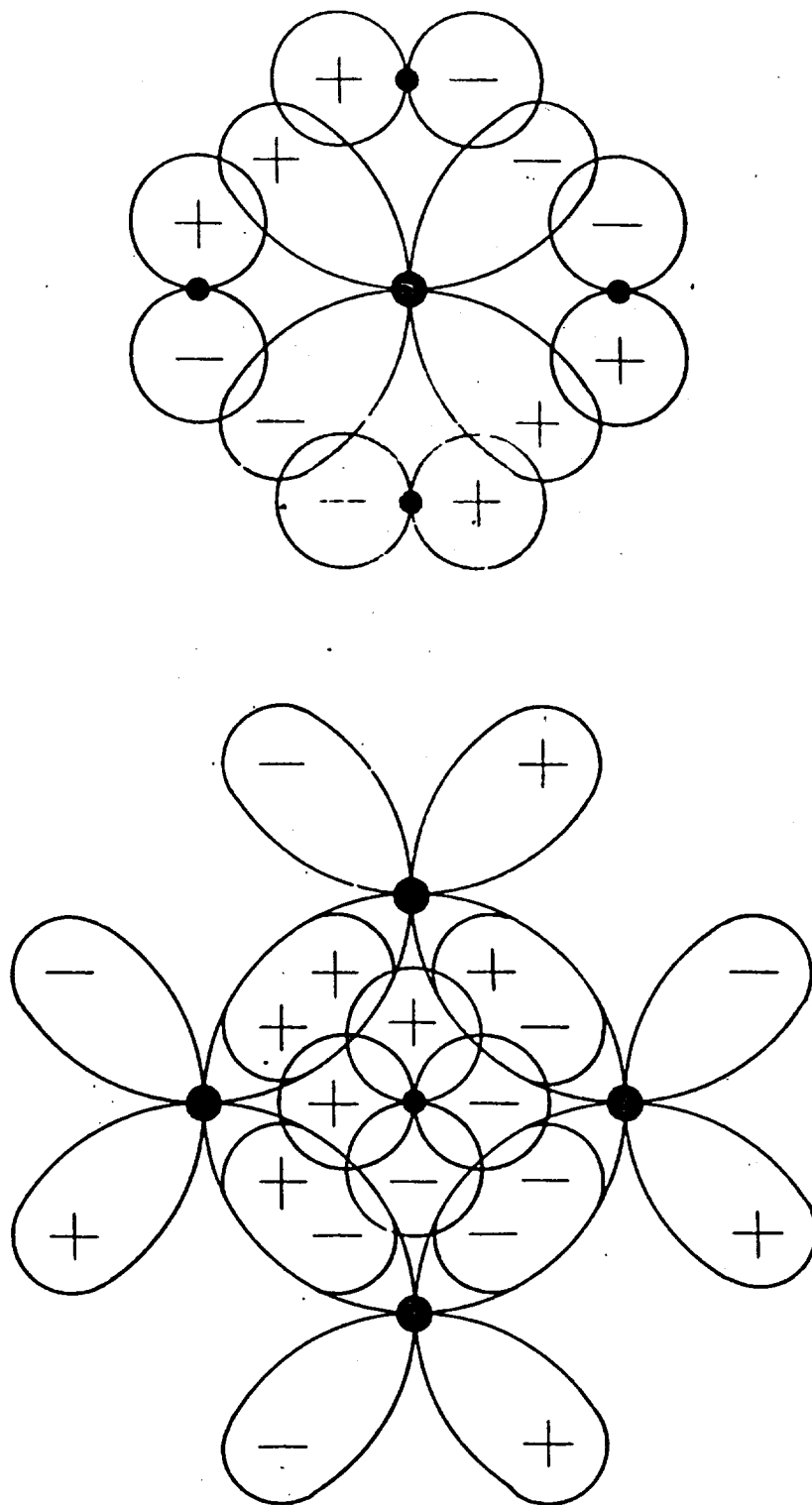
Figure 13. - pd π bonds.
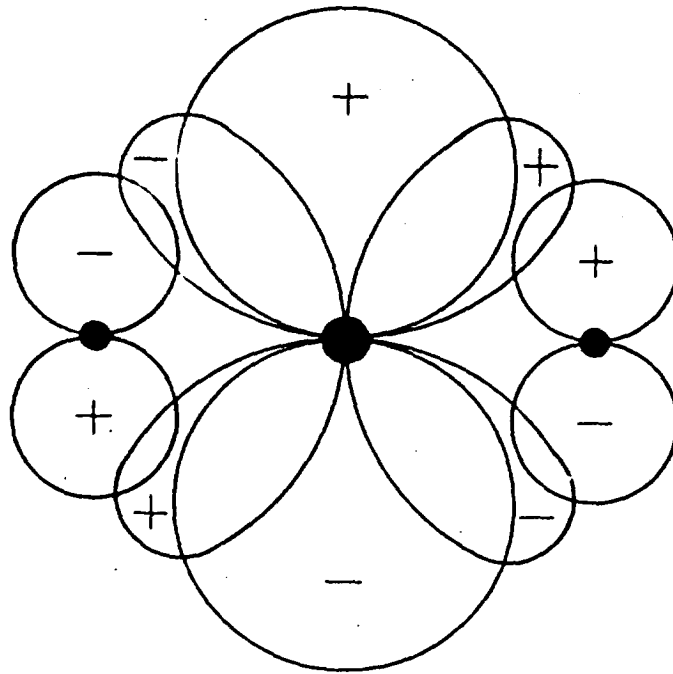
Figure 14. — DA$_6$ and AD$_6$ octahedra.

Figure 15. - 2p-3d vs 2p-4p overlaps.

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WRT:(PES)DV