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VIEWPOINTS OF STABILITY OF METALLIC STRUCTURES

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Colloquium on "Phase Stability in Metals and Alloys-March 1966.

UCRL-16250

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract W-7405-eng-48

VIEWPOINTS OF STABILITY OF METALLIC STRUCTURES

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February, 1966

Viewpoints of Stability of Metallic Structures

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ABSTRACT

The bonding in transition metals is considered and a quantitative procedure developed for the calculation of thermodynamic stability as a function of structure. The values of the enthalpies of sublimation of the bcc and hcp transition metal phases are tabulated for consideration of the possibility of stabilization of unstable structures by high pressure and for other thermodynamic applications.

INTRODUCTION

Since it is the custom in the Inorganic Materials Research Laboratory to stimulate interdisciplinary discussions, I welcome the opportunity to speak to a group as diverse as the group attending this conference. However, there are some serious problems in speaking to a heterogeneous group of this type. The difficulties may be best illustrated by an experience which we had at Berkeley. The Inorganic Materials Research Laboratory organized a symposium on metals at which one third of the speakers were physicists, one third were chemists and one third were metallurgists. As soon as the first few speakers spoke it was immediately apparent that there were great difficulties. Each of the other two groups experienced great difficulty in understanding the speaker of the other group. The vocabulary and concepts were quite unfamiliar and the communication between each of the groups was poor. There were calls for interpreters. In recognition of this difficulty the remaining speakers were urged to recognize the difficulties of communication and to present their ideas in terms that would be more generally understood. Once this difficulty had been recognized, the conference proceeded much more smoothly. However, it shortly became obvious to the members of each group that each of the other two groups had blind spots in their appraisal of metals. Each of the groups had a limited view of the problem as a whole and often did not even recognize the existence of important problems. Here we clearly had an example of three blind

men and an elephant, each describing the animal in terms of those portions that he could reach. In recognition of this previous experience, I hope today that I will be able to express my ideas in terms that will be understandable to those of you who may not have had previous experience with the types of methods that I will be using. I hope that I may be able to point out new methods of approach to the understanding of metals that may not be familiar to all of you.

One of the difficulties in maintaining good communication between the various disciplines is that there are often decided differences in the general philosophies of approach to problems. The chemist, for example, makes full use of the well established fundamental principles, but he is not content to restrict himself to areas of science which are so well developed that all properties of interest can be developed deductively from first principles. The chemist has developed a number of successful procedures that have allowed him to combine our present knowledge of the fundamental principles with various semi-empirical approaches that have carried him far beyond the reach of purely deductive processes. For example, for most molecules it is still out of the question to hope for a detailed and accurate solution of Schrodinger's equation to describe the properties of molecules. The realistic chemist is not content to limit himself to the very few molecules which can be treated accurately by rigorous quantum mechanical treatments.

A general description of the type of method used can be given in the following terms. We know that the interactions of the electrons

with one another and with the nuclei are responsible for the properties of materials. These interactions are very complex and we do not have the means of working them out in detail. However, it is recognized that certain properties are closely enough related that many of the complex interactions among the electrons affect both of the properties in a similar way. In some instances, one of these properties can be determined experimentally relatively easily, whereas the other property may be very difficult to determine experimentally. By recognizing that the influence of the electronic interactions upon the two properties have much in common and that the difference in the behavior of the two properties cancels out a great portion of the complex electronic interactions, one may often find relatively simple correlations between the variations of these two properties upon variation of some fundamental parameter such as the number of bonding electrons or the type of electrons that are involved. That is the type of correlation that I wish to present today.

In trying to develop such a correlation, it is important to have some physical picture or some type of model to serve as a guide in developing the correlation. Chemists generally use one of two starting models for treating bonding. They may be termed the molecular orbital method and the valence bond method. Even though these two methods are not consistent with one another in their simplest form, we do know that with suitable refinements, both methods must yield the same results. However, it is not possible to use either method in full refinement and it is found that for some properties one model is more

useful than the other whereas for other properties it is reversed. Often the two approaches are most usefully combined to get a more complete understanding of chemical behavior. For example, in my research work on the thermodynamic properties of high-temperature gases, it is important to be able to predict the ground and low-lying electronic states of diatomic molecules. The molecular orbital approach is an extremely useful one to predict the order of electronic states. Nevertheless, it is inadequate to meet all of our needs and I have found it very useful to combine the valence bond approach where one starts with the electronic states of the separated atoms and considers the strength of bonding due to the various combinations of atomic electronic states to produce the various molecular states that are indicated by quantum mechanical correlation rules. The molecular orbital approach takes the nuclei in their final positions with the molecular orbitals already arranged in their proper order as indicated by the theory and it is a simple matter of then adding the available electrons to determine the resulting electronic state. The same ideas are used in metals. Whereas in a diatomic molecule a combination of a pair of atoms with s atomic orbitals produces a molecule with two sigma molecular orbitals, a combination of n atoms with s orbitals would produce a molecule or a crystal with n sigma orbitals which would be spread out at different energies to produce the band that we talk about in band theory of metals. This model has been a very fruitful one for the understanding of metals. It is the common model used today just as the molecular orbital model is the

common one used today for gaseous molecules when one is interested in the distribution of electronic states. However, just as it is useful in dealing with gaseous molecules to supplement the molecular orbital theory with valence bond theory which goes back to the separated atoms, it turns out likewise to be of value in understanding more of the detail of metallic interactions to consider the valence bond approach.

In its simplest form the valence bond theory requires that there be unpaired electrons in the separated atoms which can pair with one another to form an electron pair bond between the atoms as the atoms are combined. Thus for Cl atoms with the electronic configuration s^2p^5 for the valence electrons of the ground state, only one unpaired electron is available for bonding because of the Pauli principle and the diatomic molecule Cl_2 with one electron pair bond is formed. The sulfur atom with electronic configuration s^2p^4 can use two electrons for bonding and form rings with two electron pair bonds per atom. Phosphorus (s^2p^3) forms a structure with puckered planes in which each P atom forms three electron pair bonds. Silicon atoms with the configuration s^2p^2 for the ground state introduce a new consideration. The ground state has only two unpaired electrons and only two bonds can be formed to each atom. However there is an excited electronic configuration sp^3 which has four unpaired electrons and can therefore make four electron pair bonds in the diamond structure. The promotion energy[1] of 95 kcal required to convert the ground state to the ^5S state with configuration sp^3 is more than offset by the energy of

two additional bonds and silicon does form the four-coordinated diamond structure. The previously considered elements, P, S, and Cl, had no possibility of unpairing electrons by promotion without exciting to the next main shell which would require a prohibitive promotion energy that could not be offset by additional bonding energy.

If one examines the actual processes taking place as silicon atoms, for example, approach one another, it could actually be described in terms of gradually increasing interactions as the atoms approach one another which would change the degree of configuration interaction and the relative energies of the different states to result, finally at close approach, in the stabilization of the sp^3 configuration. Rather than treat this complex process over the entire range of the approach of the atoms, it is much simpler to first prepare the atom in a valence state, that is to put in sufficient energy to promote the Si atom from the ground electronic state to the appropriate excited electronic state that would have the maximum number of electrons available for bonding, and then to bring those properly prepared valence states of the atom together to produce the final electronic structure of the solid. From the laws of thermodynamics we know that the energy or enthalpy changes must be the same by either of the processes described. The two step process by way of a valence state essentially breaks up a complex process into two much simpler processes.

The electrons which bind these non-metals together are the same glue that bind the metals together and the same procedure would be expected to be applicable to metals. For example, atomic Be, Mg, Zn, and Cd all have a ground electronic state in which there are no unpaired electrons. If the ^1S ground state were the only possibility, one would expect these elements to be very weakly bonded. They would be somewhat more strongly bonded than the rare gases because of the greater polarizability of the pair of s electrons but nevertheless very weakly bonded. In actual practice the bonding is much stronger than one would expect from consideration of only the ground electronic state. In terms of the valence bond model, one would describe the bonding in terms of the two step process by first promoting the ^1S state to a ^3P state in which there is one unpaired s electron and one unpaired p electron. Then the atoms in the ^3P valence state are brought together to produce a hexagonal close-packed structure in which there is an equal number of bonding s electrons and bonding p electrons.

For the transition metals the process is more complex in that there are s, p, and d electrons to be considered. This added complication has made it difficult to relate crystal structure to electronic structure. It has been long accepted since Hume-Rothery established the relationship[2] between numbers of electrons per atom and structures of many intermetallic compounds that there must be in many cases a strong correlation between the number of electrons per atom and the

types of crystal structures just as there was strong correlation between the structures of Cl, S, P, and Si and the number of electrons per atom.

Many years ago Niels Engel[3] proposed a similar correlation for all of the metals. Namely that the body-centered cubic structure is to be correlated with an electron configuration approximating the configuration $d^{n-1}s$. When the valence state corresponds to one s and one p electron ($d^{n-2}sp$), the hexagonal close-packed structure is expected and when the valence state corresponds to one s and two p electrons, the face-centered-cubic structure is expected. This correlation was not well accepted when originally proposed, but this correlation and the application of it as he suggested provides a very simple way of predicting a great deal of the behavior of metals. In the almost two decades since he presented his ideas, there has been a tremendous expansion in the gathering of data and it has turned out that these new data have very largely substantiated the predictions that come about through the application of the Engel theory. I have written three papers[4,5,6] in recent years which have reviewed the evidence and they show that this correlation is indeed extraordinarily effective. Not only does it allow one to correctly predict the structures of most of the pure metals, but it also allows the correct prediction of most of the structures and composition ranges of the various intermetallic phases which arise in alloy systems.

The first figure will illustrate the application of the valence bond model in terms of Engel's correlation. Here we see the relative promotion energies of the $d^{n-1}s$ and the $d^{n-2}sp$ electronic configurations for the transition metals of the second transition series, where n is the total number of valence electrons. There are other low lying electronic configurations for these elements for which not all of the electrons are unpaired, for example, the $d^{n-2}s^2$ configuration. The valence model would require that we take only those configurations with all of the valence electrons unpaired for the left hand side of the transition series where the promotion energies are small compared to the bonding energies. Another way of putting this is that the resulting levels in the metal which correlate with the configurations involving paired s electrons, which must be localized on the atom and not used in bonding between the atoms, would be relatively high in energy and would not be filled whereas levels of configurations involving all of the electrons unpaired in the valence state, and therefore completely available for bonding in the metal, would lie much lower in energy and be the ones to be filled with electrons. Both the $d^{n-1}s$ and $d^{n-2}sp$ configurations in Figure 1 have all the various electrons unpaired and free for bonding. There are some differences in the bonding ability of d electrons compared to the s and p electrons that will be discussed in detail shortly, but if we ignore these differences we can still use the data shown in Figure 1 to qualitatively predict the relative stability of the

bcc and hcp structures for these elements. The energies are presented as bands or areas since there are a number of states corresponding to a given electronic configuration. The range of energies are those of the electronic states of highest multiplicity which correspond to the indicated electronic configurations. It can be seen that for the first three metals, strontium, yttrium and zirconium, the two configurations lie close enough together in energy so that one might expect that the bcc ($d^{n-1}s$) and hcp ($d^{n-2}sp$) structures would be close together in energy. This is found experimentally to be the case. All three of these elements have a hcp structure which converts to bcc structure at higher temperatures. Since the bcc structure has a coordination number of eight compared to a coordination number of twelve for the hcp structure, the bcc phase would be expected to have more vibration and a greater entropy and therefore would be the one to become stabilized at the higher temperatures. For niobium and molybdenum it can be seen that the electronic configuration $d^{n-2}sp$ is so highly promoted compared to the configuration with only one s electron that one would predict that the hcp structure would be considerably unstable compared to the bcc structure. This again is in agreement with the experimental observations since only the bcc structure is known for niobium and molybdenum at all temperatures and pressures. Similar comparisons for the other transition metals indicate that the predictions that can be made with the spectroscopic data that are available are in agreement with the available experi-

mental observations. To allow comparison between the predictions of the calculations to be presented below and the experimental observations, the crystal structures of the elements are presented in Table I.

There are then two steps in the application of the methods that I wish to describe today. First we must examine[1] the available electronic configurations for the gaseous atoms and consider the promotion energies[1] required to obtain configurations which have their electrons completely available for bonding (for elements of the first six groups) and then compare the bonding energies of each of the configurations to determine which yields the lowest levels in the metal. If the valence state which contributes to the lowest levels in the metal is one which involves only one s electron, then the Engel correlation would predict a bcc structure. If the valence state contributing to the bulk of the low lying levels in the metal is one involving sp electrons, one would expect the hcp structure. In the discussion groups that are scheduled for this meeting, the question of why a given structure should result from a given electronic configuration will be discussed in more detail. The theory is more difficult to apply to metals than to simple gaseous molecules where the structures resulting from various combinations of s, p, and d orbitals has been well worked out. For the metals the situation is complicated in that one must consider not only nearest neighbors but more distant neighbors. For example, in comparing the hcp and the ccp structures, it is clear that one could not make any

predictions about the relative stabilities of these two structures on the basis of any model that depended only upon nearest neighbor interactions. However, more complex calculations have been carried out by Altmann, Coulson and Hume-Rothery[8] which show that characteristic structures are to be associated with specific electronic configuration.

One can now use the spectroscopic data in a more quantitative manner by using the experimental promotion energies required to achieve each of the two electronic configurations under consideration here together with the experimental enthalpies of sublimation to determine the bonding energies that result when the gaseous atoms in the corresponding valence state are condensed to the solid metal. The enthalpies of sublimation of the metals have been taken from published tabulations.[4,7] The promotion energies[1] for the $d^{n-2}sp$ electronic configuration are given in Table II. Table III shows the corresponding promotion energies[1] from the ground electronic state of the gaseous atoms to the electronic configuration $d^{n-1}s$. The second numerical entry below each element is the promotion energy which would correspond to the configuration $d^{n-1.5}sp^{0.5}$ which would be the average of the promotion energies for the configuration with one s electron and the configuration with one s and one p electron. The second value is tabulated because the bcc structure is observed up to a total of one and a half electrons of the s or p type per atom and thus the range of promotion energies from that for one s electron to that for one and a half s, p electrons must be considered for quantitative

treatment of the data for bcc structure. The calculation of stabilities of bcc structure based on the two configurations will be illustrated later and can be used to determine which configuration is the most appropriate. Generally throughout the periodic table one expects the bonding energies of s or p electrons to decrease with increasing internuclear distances as one goes down in the periodic table. One would expect the bonding energies to increase to the right in the periodic table because of increasing nuclear charge. Figure 2 illustrates data for bonding energies of metals of the second transition series. The top curve is a curve of bonding energy due to an s or p electron going from Sr to Cd. The values for Sr and Cd can be fixed directly since they both have hcp structures corresponding to sp electronic configurations. The smooth curve drawn in between corresponds to the expected variation of bonding energy as nuclear charge is increased. For each of the elements in this series, the bonding energy was calculated from the combination of sublimation enthalpies and promotion energies. The contribution of the s or p electrons was subtracted, the number of s and p electrons being determined by the structure. The resulting bonding energy was assigned to the remaining d electrons and the lower curves in Figure 2 correspond to the bonding energy per d electron available for bonding, (i.e., the remaining bonding energy divided by the number of unpaired d electrons). The characteristic curve that is shown here is typical of the curves in Figure 3 and 4 found for the other transition series, in that the bonding effectiveness of a d electron decreases as the number of d bonds increases reaching a minimum at the maximum of five d bonds per atom, apparently due to interference between the d bonds

when there are too large a number of d bonds. The x's indicates the experimental points derived from hcp structures, the circles indicate the values derived from bcc structures. The bonding energy of an electron is largely independent of the particular structure and one can draw a curve that can be used for predicting the bonding in yet unobserved phases of these metals with either the bcc or hcp structures. For example, for hcp niobium which has never been observed, one could predict the stability of such a phase by calculating the bonding energy that would result from the configuration d^3sp by multiplying by two the bonding energies given in Figure 2 for an s or p electron of niobium and multiplying by three the bonding energy for a d electron when there are a total of three d bonds per atom as indicated by the ordinate at the bottom of Figure 2. This bonding energy for three d electrons added to contribution of the two sp electrons yields the total bonding energy for the valence state d^3sp condensing to produce hcp niobium. From this bonding energy must now be subtracted the promotion energy given in Table I for the configuration d^3sp to yield an atomization energy of 158 kcal for hcp niobium. A similar procedure for the configuration d^4s yields an atomization energy of 173 kilocalories for the bcc structure which indicates that the hcp structure of niobium is quite unstable. A more detailed treatment to be presented below shows that a slightly less unstable hcp Nb is calculated using the configuration $d^{3.3}sp^{0.7}$.

This procedure has been carried out for all the transition metals and Table IV yields the bonding energies when the indicated valence

states of the gaseous atoms are combined to form hcp solids. Table V indicates the corresponding bonding energies for the formation of bcc structures. These can then be combined with the promotion energies given previously to calculate the heats of sublimation of either bcc or hcp structures for all of the transition metals except for Rh and Pd where only rough estimates can be given for the hcp structure since the spectroscopic data for the $d^{n-2}sp$ configurations are incomplete or lacking for these two elements. Before carrying out the calculations of the heats of sublimation given in Table VI, we must examine in more detail the process of bonding for transition metals. It might be useful at this point to translate from valence bond terminology to molecular orbital and electronic band terminology. We have been speaking of the groups of electronic levels of a gaseous atom which correspond to a given electronic configuration. In some instances, such as shown for yttrium in Figure 1, the energies of two configurations are so close that the electronic states are actually intermingled. This is also shown in Table VII where the ranges of energy of the sublevels of each electronic state of each electronic configuration of Y are tabulated. When we consider a diatomic molecule from the molecular orbital point of view, we similarly find instances of molecular orbitals with similar energies such that the molecular electronic levels corresponding to each configuration are intermingled. Also, typically the electronic states corresponding to a given molecular orbital correlate to different electronic configurations of the atoms.

When the gaseous atoms are condensed to the metal, the electronic configurations that participate in bonding are lowered in energy to produce a sequence of low lying levels or bands that will be filled by electrons. When two electronic configurations are close in energy, there will be intermingling of levels and strong configuration interaction and the bands can not always be uniquely described in terms of an integral electronic configuration. For example, in Table V, the three valence electrons of Sc, Y, and La are designated as being 50% d, 33% s, and 17% p or the $d^{1.5}sp^{0.5}$ configuration. This recognizes that the d^2s and dsp configurations are so close together that the lower levels of the electronic band, that will be filled, will be characterized as originating approximately equally from the two configurations. It was noted earlier that the bcc structure is expected not only for a metal with a $d^{n-1}s$ electronic configuration but that the bcc structure persists with increasing contribution from the $d^{n-2}sp$ configuration up to a limit of $d^{n-1.5}sp^{0.5}$. This is discussed in reference 5 in detail for the transition metal alloy systems. It might be useful at this point to examine some alloys systems for the implications of a limiting electronic configuration.

Figure 5 is a multi-dimensional phase diagram of the type given in reference 5. A horizontal line between Mo and Os, for example, represents a projection of the binary Mo-Os system along the temperature axis such that the composition range of each phase region represents the maximum extent at the optimum temperature. Thus the

I phase region or bcc structure extends from Mo to 20 atomic % Os, the A15 or Cr_3Si structure has a narrow composition range around Mo_3Os, the σ phase extends from 30 to 37 atomic % Os, and the area labeled II corresponds to the hcp phase region from 48 to 100 atomic % Os. A horizontal line drawn half-way between Re and Os would represent the sequence of phase regions resulting from adding Mo to an equimolal mixture of Re and Os. The Engel theory indicates that the diagram of this type will yield simple trends in solution behavior. The elements on the right hand side are the adjoining elements of the same transition series to minimize the effect of variation of atomic size and of internal pressure and thus isolate the effect of electron concentration. The ordinate on the right hand side is, in effect, the number of electrons per atom varying from 6 for W to 10 for Pt. If a mixture of W, Re, Os, Ir, and Pt is taken and the average electron concentration computed, e.g. 7.5 valence electrons per atom, then the alloy behavior upon adding Mo to this mixture would be defined by the horizontal line from the 7.5 position half way between Re and Os. Thus the Engel theory indicates the types of diagrams that will represent a maximum of information with a minimum of space as Figure 5 is in agreement with all the reliable data available. It will be noted that the regions labeled by I(bcc), σ(β-U), χ(α-Mn), II(hcp), and III(ccp) show the behavior of electron-phases or electron-compounds. That is, they are restricted to a limited range of electron concentrations or averaged electron per atom ratios. If one were to draw isoelectronic lines or

lines of equal electron per atom concentrations, they would extend across the diagram in the manner of the boundaries of the electron phases listed above.

The implication of electron-phases in terms of free energy variation is that the relatively slow variation of free energy of the bcc phase as Os is added to Mo, for example, changes to a rapid rate of increase as the electron concentration approaches 6.5 electrons per atom. The limiting concentration will, of course, not be determined by the free energy of the bcc phase alone but also by the free energy of the saturating phase. Examination of all the available data and particularly the non-transition metal diagrams as discussed in reference 5 indicates that the Hume-Rothery limit of 1.5 s, p electrons is a reasonable limit for the bcc structure. From the free energy considerations, we recognize that the actual limits will vary somewhat depending upon the temperature, internal pressure differences, and the nature of the saturating phase and that these other factors have to be considered as secondary corrections, but Figure 5 shows that the limits of the bcc phase regions do approach closely to the $d^5sp^{1.5}$ limit. Generally the limits will fall short with the difference increasing with increasing size difference and increasing internal pressure differences as one would expect. Reference 5 discusses in more detail the methods of establishing the electron concentration limits for the various electron-phases and the methods of dealing with factors such as size and internal pressure differences which are clearly recognized as important factors in fixing the free energies in addition to electron concentrations.

Returning now to pure elements, the recognition of ranges of electron concentrations to be correlated with a given structure leaves some ambiguity as to the assignment of exact electronic configuration in some instances. We can see from the large difference in energy of the d^5s and d^4sp configurations of Mo, shown in Figure 1 or in Tables II and III, together with the bonding energies of d versus p electrons shown in Figure 2 that all the low lying levels of the electronic bands of metallic Mo will be derived almost exclusively from the d^5s configuration and there is no question of what electronic configuration to assume in chosing the promotion energy from Table V. However, we would not expect such simple behavior for Y, for example, for which the $d^{n-1}s$ and $d^{n-2}sp$ configurations are close in energy.

The relative contributions of the $d^{n-2}sp$ and $d^{n-1}s$ configurations to the bonding of the transition metals with five or less d electrons depends upon the relative bonding strengths of p and d electrons, $E_p - E_d$, as given in Figures 2-4 compared to the relative promotion energies tabulated in Tables II and III. Only a small portion of the curve of E_d versus n_d, the number of d electrons, is applicable for a given element, e.g. 0.5 electron per atom variation for the bcc structure and 0.3 electron per atom variation for the hcp structure. If that small portion is approximated as a straight line, one can set up a simple equation for the energy as a function of n_d, the number of d electrons. Differentiation of this equation to solve for the condition of minimum energy yields the equation

$$n_d = [E_{prom} - (E_p - E_d)]/S$$

where E_{prom} is the energy to promote a d electron in $d^{n-1}s$ to a p electron in $d^{n-2}sp$ and S is the rate of change of E_d with decrease in number of d electrons of the slope of the plot of E_d versus n_d in Figures 2-4. Of the quantities required to calculate n_d, E_{prom} is obtained directly from Tables II and III. The promotion energies have a range of values corresponding to the different electronic states of a given configuration. The minimum promotion energies are used for the reasons discussed in Appendix 1. The value of E_p is taken from Figures 2-4 for the particular element in question. S is obtained from the slope of E_d versus n_d in the range of n_d values that are allowed by the Engel correlation. Thus all of the quantities are uniquely fixed at the start of the calculation except E_d which will vary with n_d. If we use bbc Zr as an example, the first approximation of E_d= 39 kcal corresponding to a guess of n_d = 2.5 electrons yields n_d = [28 -(51-39)]/5.8 = 2.75. The second approximation uses E_d = 38 kcal and n_d converges to 2.7 corresponding to the configuration $d^{2.7}sp^{0.3}$. In Appendix 1 where the details of the arithmetic calculations are presented, atomizations energies of the $d^{2.5}sp^{0.5}$, $d^{2.7}sp^{0.3}$, and d^3s configurations are calculated to be 145, 146, and 146 kcal, respectively, illustrating the shallow nature of the minimum of energy in this example.

For transition elements with five or more d electrons, the promotion of a d to a p electron releases two electrons for bonding and the energy varies as the sum of $E_p + E_d$ in contrast to the difference $E_p - E_d$ for elements with five or less d electrons. For these elements, much higher promotion energies can be offset, particularly to the far right of the transition series where the number of bonding d electrons is small and the sum $E_p + E_d$ is large. Differentiating the energy equation to obtain the minimum energy as above yields

$$n_d - 5 = [E_{prom} - (E_p + E_d)]/S$$

where n_d is the total number of d electrons and not the number of bonding d electrons shown in Figures 2-4. For $n_d > 5$, the number of bonding d electrons will be $10 - n_d$.

The procedure outlined above and given in more detail in Appendix 1 was used to characterize the optimum electronic configurations of the transition metals. In many instances, the energy varied clearly across the configuration range with the calculated minimum energy outside the range allowed by the Engel correlation since the above equations do not incorporate any terms to produce an increase in free energy at the limits set by the Engel correlation. Configurations could clearly be assigned as the limiting configuration of lowest energy. For elements with the minimum energy at a configuration intermediate between the limiting configurations, the atomization energies were often almost identical for either limit. Since there

was little effect upon the calculated energy, the entry in Tables IV and V was chosen to minimize the number of starred entries corresponding to an element with a different electronic configuration than the other elements of the same group. In Figures 2-4, values are plotted for both of the limiting configurations when they are of closely the same stability.

With the optimum configurations clearly established, one may proceed to the calculation of atomization energies of the various structures. For example, we previously calculated the atomization energies of bbc and hcp Nb on the basis of the d^4s and d^3sp configurations. The d^4s configuration is the optimum configuration for bbc Nb and the atomization energy of 173 kcal is unchanged, but the optimum configuration of hcp Nb is the $d^{3.3}sp^{0.7}$ configuration which yields the valence state bonding energy of 197 kcal listed in Table IV and an atomization energy of 163 kcal after subtraction of promotion energy to indicate that hcp Nb is unstable by 10 kcal relative to bcc Nb. Table VI presents the results for the other transition metals.

Table VI in agreement with Table I shows the universal occurrence of a stable bcc structure for all of the transition metals of the first six groups. It is of interest to comment on the primary factor responsible for the widespread occurrence of the bcc structure. It could be due to either a preference for d bonding over p bonding or to difference in promotion energies of the $d^{n-1}s$ and $d^{n-2}sp$. Examination of Figures 2-4 and Tables II and III show that except for Ca and

Sr, the promotion energy alone is the primary factor. In fact the greatly reduced bonding energy of the d electrons compared to the bonding energy of the p electrons when one or more d electrons are involved in bonding tends to stabilize the hcp structure, but in no instance is this stabilization sufficient to wipe out the advantage of the lower promotion energy of the $d^{n-1}s$ configuration and to make the bcc structure unstable at all temperatures.

On the right hand side of the periodic table, the bonding energies of Figure 3 yield the results of Table VI that hcp Mn, Fe, and Co are close in energy to the bcc structures. It is difficult to predict the entropies of these phases because of the magnetic contributions. The higher atomization enthalpy of bcc Fe is sufficient to insure its stability relative to hcp Fe at low pressures. However, bbc Co has a smaller atomization enthalpy than hcp Co by two kilocalories which is too large to be overcome by any likely entropy difference. Mn is one of the unique elements like U and Pu for which several different electronic configurations yield closely the same stabilities. The values in Table VI indicate that α-Mn and β-Mn have a substantial contribution from the d^5sp configuration but that there must be atoms with d^4sp^2 and d^6s configurations maintaining separate identities rather than averaging electron configurations with their neighbors.

The experimental spectral data clearly confirm that the bcc and hcp structures are to be correlated with $d^{n-2}s$ and $d^{n-2}sp$ configurations and the theoretical calculations[8] are also in agreement with

the Engel correlation. For the ccp structure, the theoretical calculations[8] indicate correlation with $d^{n-3}p^3$ rather than with $d^{n-3}sp^2$ that Engel has suggested. Table VII presents the spectral data for yttrium, for which all expected electronic states of high multiplicity of the possible configurations involving 4d, 5s, and 5p electrons are known except for the d^2p ^4P state and the states of the p^3 configuration. The comparison of $dsp-ds^2$, s^2p-sp^2, d^2s-d^2p, $dsp-dp^2$, differences indicate that the p^3 configuration would be expected well above 100 kcal. Examination of the spectral data for the other elements, for which data are less complete than Y, also indicate that the $d^{n-3}p^3$ configuration has too high a promotion energy to make a significant contribution to the metallic bonding. The theoretical calculations might be reconciled with the spectral data by using the $d^{n-1}p$ configuration since the calculations indicated that mixtures of d^n and $d^{n-3}p^3$ would yield the ccp structure. Except for La which has an unusually low promotion energy of 50 kcal for the d^2p configuration, the promotion energies for the transition elements range from over 60 to 120 kcal. Accurate comparison with the $d^{n-3}sp^2$ configuration since Y is the only transition element for which data on this configuration are known. This is due to the fact that transitions from the ground electronic state to states of this configuration are very weak because they involve multiple electron jumps and violate other spectral selection rules. However, as shown in Table VII for Y, it is expected that the sp^2 configuration will

not lie below the $d^{n-1}p$ configuration. However only to the left of the periodic table, where the d electron bonding is as strong or stronger than the s, p bonding, will the $d^{n-1}p$ configuration have any advantage over the $d^{n-3}sp^2$ configuration. On the right hand side of the periodic table, the $d^{n-3}sp^2$ configuration has a very large advantage in valence state bonding energy over the $d^{n-1}p$, $d^{n-1}s$, and $d^{n-2}sp$ configurations since the $d^{n-3}sp^2$ configuration produces the greatest unpairing of electrons.

Thus it is possible that the $d^{n-1}p$ configuration might play a role in stabilizing fcc Ca, Sr, and La, but the bonding energies required do not seem reasonable. Due to the fact that all configurations that would be considered for the elements of the first six groups have all of the valence electrons unpaired in the valence state, the possibility of significant contribution to the bonding by either $d^{n-1}p$ or $d^{n-3}sp^2$ for the other metals of the third through sixth groups can be excluded. For example, from the data of Figure 2 and Table VII, one calculates that fcc Y is unstable by 20 kcal compared to hcp or bcc Y. It is difficult to reach a definite decision for La due to uncertainty of spectral data for Sc and La. One method of extrapolation would estimate the sp^2 promotion energy for La to be much lower than Y, perhaps around 50 kcal and another method would estimate about the same promotion energy for Y and La. Also the estimation of the bonding energy of La in the sp^2 valence state is difficult because the lanthanide contraction creates a discontinuity between La and Hf.

Calculation of valence state bonding energies for the metals on the right hand side of the transition series indicate that the fcc structure with the sp^2 configuration or with the lower limit indicated by the Engel correlation of $d^{n-2.5}sp^{1.5}$ would be stable with respect to bcc and hcp structures with $d^{n-3}sp^2$ promotion energies of 110 to even 190 kcal. Examination of the data for the $d^{n-3}s^2p$ configuration and the trends across the transition series indicates that the promotion energies can be expected to fall in that range. When more spectral data become available for the transition metals, it should be possible to carry out calculations for the ccp structure as in Table VI.

This work was performed under the auspices of the United States Atomic Energy Commission.

APPENDIX 1

Calculation of Atomization Enthalpies

The use of Figures 2-4 and Tables II and III to calculate atomization enthalpies will be illustrated by the example of Zr. Although the difference between the energy and the enthalpy of atomization is within the uncertainty of these calculations, the values in Figures 2-4 are designed to yield enthalpy values at 298°K. From Figure 2 it is seen that the bonding enthalpy of the d^3s valence state is 3 x 36 + 51 or 159 kcal. The promotion energy of 14 kcal from Table III then yields an atomization enthalpy of bbc Zr at 298°K. of 159-14 or 145 kcal to the ground state of the gaseous atom. For the configuration $d^{2.5}sp^{0.5}$, the bonding enthalpy is 2.5 x 39 + 1.5 x 51 or 174 kcal but the promotion energy is 28 kcal yielding an atomization enthalpy of 146 kcal. Finally the configuration $d^{2.7}sp^{0.7}$, which is the configuration that yielded the most stable solid as discussed earlier, yields a valence state bonding enthalpy of 2.7 x 37.7 + 1.3 x 51 or 168 kcal. The promotion energy of 22 kcal then yields an atomization enthalpy of 146 kcal. When the promotion and bonding energies are so balanced that the optimum configuration is centered between the limiting configurations, the variation across the range is so small that calculations carried out to fractions of a kcal are necessary to show the variation accurately. Such an accuracy is not warranted for the present purposes.

In the above calculations, the promotion energy that is used should be in principle the average promotion energy of the range of electronic states that correspond to the molecular orbitals or band levels being filled. In the calculations upon which Figures 2-4 and Tables IV and V are based, the promotion energy was taken in every case as the lowest promotion energy of the bottom level of each group of levels. As long as the difference between the lowest level and the average level does not change abruptly from one element to the next, this is quite an adequate procedure; since the use of average promotion energies rather than the lowest would increase the promotion energies and the calculated bonding energies equally. Thus the curves of Figures 2-4 would be uniformly raised. Since the observed points fall on smooth curves, there is direct evidence that there is no abrupt variation from one element to the next and no appreciable error is introduced by the calculation procedure used here.

It is interesting to note that the curves of Figures 2-4 are not only smooth but that the bcc and hcp curves fall very close to one another. Differences in additional energy obtained by hybridization and other interactions could produce differences; it is a simplification to have the bonding energies so nearly independent of structure or configuration. This makes it easier to extrapolate the use of these curves and common curves were assumed for both structures on the right hand side of the periodic table where there are data both structures are lacking. The closeness of the curves also provides a basis for using the curves to calculate values for fcc structures.

The electron bonding energies in Figure 3 are plotted against the number of bonding d electrons. In view of the magnetism of the metals from Cr to Ni, it is clear that not all of the unpaired electrons of the valence state are used in forming electron pair bonds. In fact the value of S, the rate of change of d bonding energy with the number of d electrons is so large in Figure 3 that one could calculate that Cr, for example, would have a higher bonding energy by not using one of its d electrons if the bonding of the remaining d electrons would be based on the value higher up the curve corresponding to just the number of d electrons used in bonding. By using magnetic data, it would be of interest to calculate the plot of Figure 3 on the basis of the actually bonding electrons. However, for the present purposes, Figure 2 is adequate.

TABLE 1

Crystal Structures of the Elements[a]

Li I	Be II	B * *											C IV [f]	N [b]	O [b]	F [c]
Na I	Mg II	Al III											Si IV	P [e]	S [d]	Cl
K I	Ca I III	Sc I II	Ti I II	V I	Cr I	Mn I III β χ	Fe I III I	Co III II	Ni III	Cu III	Zn II	Ga A11	Ge IV	As	Se	Br
Rb I	Sr I II III	Y I II	Zr I II	Nb I	Mo I	Tc II	Ru II	Rh III	Pd III	Ag III	Cd II	In (III)[g]	Sn A5 IV	Sb	Te	I
Cs I	Ba I	La I III II	Hf I II	Ta I	W I	Re II	Os II	Ir III	Pt III	Au III	Hg A10	Tl I II	Pb III	Bi	Po	At
Fr	Ra	Ac														

Ce I III II	Pr I II	Nd I II	Pm	Sm I (II)[g]	Eu I	Gd I II	Tb I II	Dy I II	Ho I II	Er I II	Tm I II	Yb I III	Lu I II
Th I III	Pa *	U I σ (II)	Np I **	Pu I * III ***	Am ? II	Cm ? II	Bk	Cf	Es	Fm	Md		Lw

[a]I: Body centered cubic, A2. II: Hexagonal close packed, A3. III: Cubic close packed, A1. IV: Diamond, A4. Asterisk denotes complex structure. [b]Diatomic molecules with double or triple bonds. [c]Diatomic molecule with a single electron pair bond. [d]Atoms which form two single bonds per atom to form rings or infinite chains. [e]Three single bonds per atom, corresponding to a puckered planar structure. [f]The graphite structure where one resonance form consists of two single and one double bond per atom. [g]Parentheses indicate slight distortions. The structures are listed in order of temperature stability except for metastable diamond.

Table II

Promotion Energies of $d^{n-2}sp$ Valence State in Kcal/Mole

Ground State Configurations										
s^2	ds^2	d^2s^2	d^3s^2 except *	d^5s except *	d^5s^2	d^6s^2 except *	d^7s^2 except *	d^8s^2 except *	$d^{10}s$	$d^{10}s^2$
Mg 63										
Ca 43	Sc 45-46, 53	Ti 45-54, 72-80	V 47-54, 81-88	Cr 71-80	Mn 53	Fe 55-70	Co 67-76	Ni(d^8s^2) 74-87	Cu 113-128	Zn 92-94
Sr 41-43	Y 43-49, 54	Zr 42-57, 66-74	Nb*(d^4s) 48-61, 74-86	Mo 80-93	Tc 47-50	Ru*(d^7s) 72-93	Rh*(d^8s) (95)-	Pd*(d^{10}) <145-	Ag 161-185	Cd 86-91
Ba 35-39	La 38-46, 50-52	Hf 51-79, 85-95	Ta 49-99	W*(d^4s^2) 55-85	Re 54-68	Os 67-(90)	Ir 75-109	Pt*(d^9s) 86-160	Au 121-160	Hg 108-126
Ra 37-48	Ac 39-68									

Table III

Promotion Energies of $d^{n-1}s$ and $d^{n-1.5}sp^{0.5}$ Valence States in Kcal/Mole

Ground State Configurations									
s^2	ds^2	d^2s^2	d^3s^2 except *	d^5s except *	d^5s^2	d^6s^2 except *	d^7s^2 except *	d^8s^2 except *	$d^{10}s$
Mg 137 100									
Ca 58 51	Sc 33, 51 39-43, 48-52	Ti 19,40 32-60	V 6-7 26-48	Cr 0 36-40	Mn 49-50 51-52	Fe 20-23, 50-51 38-47, 53-61	Co 10-15, 43-46 39-61	Ni 1-5 37-46	Cu 0
Sr 52 47	Y 31-33, 44 37-49	Zr 14-17, 31-32 28-53	Nb*(d^4s) 0-3 24-45	Mo 0 40-47	Te 7-12 27-31	Ru*(d^7s) 0-9, 25-27 36-60	Rh*(d^8s) 0-10, 26-31	Pd*(d^{10}) 19-29	Ag 0
Ba 26-27 30-33	La 8-12, 21-22 23-37	Hf 40-51, 59-64 46-79	Ta 28-38 39-69	W*(d^4s^2) 8 32-47	Re 34-49 44-58	Os 15-37, 44-(51) 41-52, 56-	Ir 8-34, 37-48 42-78	Pt*(d^9s) 0-29 43-	Au 0
Ra 37-42 38-45	Ac (15-20), 26-35 26-51								

Note: The numerical entry below the symbol of an element gives values for the $d^{n-1}s$ valence state. Where a second entry is given, it is for the $d^{n-1.5}sp^{0.5}$ valence state.

Table IV

Bonding Energies of the $d^{n-2}sp$ Valence State in the Hexagonal-Close-Packed Structure in Kcal/Mole.

Number of Bonding Electrons Per Atom										
2	3	4	5	6	7	6	5	4	2.4	2
Mg										
98										
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu*	Zn
(84)	136	158	(165)	(158)	(121)	154	169	(171)	(135)	124
Sr	Y	Zr	Nb*	Mo*	Tc	Ru*	Rh*	Pd*	Ag*	Cd
80	144	188	(197)	(198)	205	205	(189)	(165)	(130)	114
Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au*	Hg
(74)	142	198	(230)	(244)	241	255	(234)	(215)	(140)	(123)

Bonding Energies of the $d^{n-2}sp$ Valence State in the H. C. P. Structure in Kcal per Bonding Electron.

Mg										
49										
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu*	Zn
(42)	45	40	(33)	(26)	(17)	26	34	(43)	(56)	62
Sr	Y	Zr	Nb*	Mo*	Tc	Ru*	Rh*	Pd*	Ag*	Cd
40	48	47	(39)	(33)	29	38	(43)	(49)	(54)	57
Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au*	Hg
(37)	47	50	(46)	(41)	34	43	(47)	(54)	(58)	(62)

* Indicates that bonding energy is given for $d^{n-1.7}sp^{0.7}$ valence state. The number of bonding electrons per atom for Ru*, Rh*, and Pd* are, respectively, 5.4, 4.4, and 3.4. For Cu*, Ag*, and Au*, the $d^{9.3}sp^{0.7}$ valence state has 2.4 bonding electrons per atom.

Table V

Bonding Energies of the $d^{n-1}s$ or $d^{n-1.5}sp^{0.5}$ Valence States in the B.C.C. Structure in Kcal/Mole.

	Valence State and Number of Bonding Electrons Per Atom										
1	2	3	4	5	6	6	5	4	3	2	1
s	$d^{0.5}sp^{0.5}$	$d^{1.5}sp^{0.5}$	$d^{2.5}sp^{0.5}$	$d^{3.5}sp^{0.5}$ except *	$d^{5}s$ except *	$d^{5.5}sp^{0.5}$	$d^{6.5}sp^{0.5}$	$d^{7.5}sp^{0.5}$ except *	$d^{7.5}sp^{0.5}$ except *	$d^{9}s$	$d^{10}s$
Na											
26											
K	Ca	Sc	Ti	V	Cr*($d^{4.5}sp^{0.5}$)	Mn	Fe	Co	Ni		Cu
21.5	92	129	144	149	131	119	138	(139)	(135)		(61)
Rb	Sr	Y	Zr	Nb*($d^{4}s$)	Mo	Tc		Ru*($d^{7}s$)	Rh*($d^{8}s$)	Pd	Ag
19.5	85	138	174	173	157	(179)		(153)	(131)	(102)	(56)
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt		Au
19	73	126	192	226	211	(228)	(218)	(197)	(167)		(59)

Bonding Energies of the $d^{n-1}s$ or $d^{n-1.5}sp^{0.5}$ Valence States in the B.C.C. Structure in Kcal Per Bonding Electron

Na											
26											
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni		Cu
22	46	43	36	30	22	20	28	(35)	(45)		(61)
Rb	Sr	Y	Zr	Nb	Mo	Tc		Ru	Rh	Pd	Ag
20	43	46	44	35	26	(30)		(38)	(44)	(51)	(56)
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt		Au
19	37	42	48	45	35	(38)	(44)	(49)	(56)		(59)

Table VI

ΔH°_{298} of Sublimation of BBC and HCP Phases of the Transition Metals; kcal/mole.

	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
BCC	41	90	112	123	95	68	100	(100)	(98)	(61)
HCP	(41)	91	113	(118)	(87)	(68)	(99)	102	(97)	(56)
	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
BCC	38	101	146	173	157	(152)	(153)	(131)	(83)	(56)
HCP	39	102	146	(163)	(142)	158	155			
	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au
BCC	43	103	146	187	203	(184)	(177)	(155)	(124)	(59)
HCP	(41)	104	147	(181)	(189)	187	188	(159)	(129)	(55)

Note: Values in parentheses are for phases that are not stable at 1 atm pressure.

Table VII

Relative Energies in Kcal of States of Highest Multiplicity of the Electron Configurations of Y

d^2p	^4D, ^4S, (^4P)	103 to 107
dp^2	^4D, ^4F, ^4P	97 to 100
sp^2	^4P	66 to 67
d^2p	^4G, ^4F, ^4D	53 to 54, 59 to 61, 64 to 65
d^3	^4F, ^4P	53 to 54, 60 to 61
dsp	^4F, ^4D, ^4P	12 to 15, 16 to 18, 23
d^2s	^4F, ^4P	0 to 2, 12 to 13
s^2p	^2P	- 1 to + 2
ds^2	^2D	-31 to -30

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Figure Captions

Figure 1. Relative stabilities of $d^{n-1}s$ and $d^{n-2}sp$ electronic configurations for transition metals of the second transition series.

Figure 2. Valence state bonding enthalpy, Kcal/mole per electron.

Top curve - $E_{s,p}$, bonding enthalpy of 5s or 5p electrons, versus element.

Bottom curve - E_d, bonding enthalpy of 4d electrons, versus number of unpaired d electrons.

Figure 3. Valence state bonding enthalpy, Kcal/mole per electron.

Top curve - $E_{s,p}$, bonding enthalpy of 4s or 4p electrons, versus element.

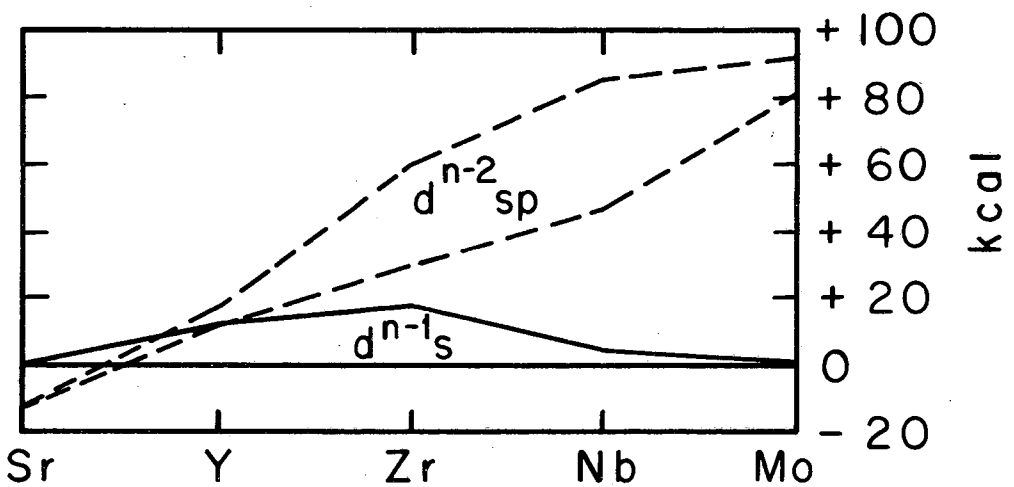
Bottom curve - E_d, bonding enthalpy of 3d electrons, versus number of unpaired d electrons.

Figure 4. Valence state bonding enthalpy, Kcal/mole per electron.

Top curve - $E_{s,p}$, bonding enthalpy of 6s or 6p electrons, versus element.

Bottom curve - E_d, bonding enthalpy of 5d electrons, versus number of unpaired d electrons.

Figure 5. Multicomponent phase diagram of Mo with third transition series metals, W to Pt, projected along the temperature axis.



MUB-8895

Fig. 1

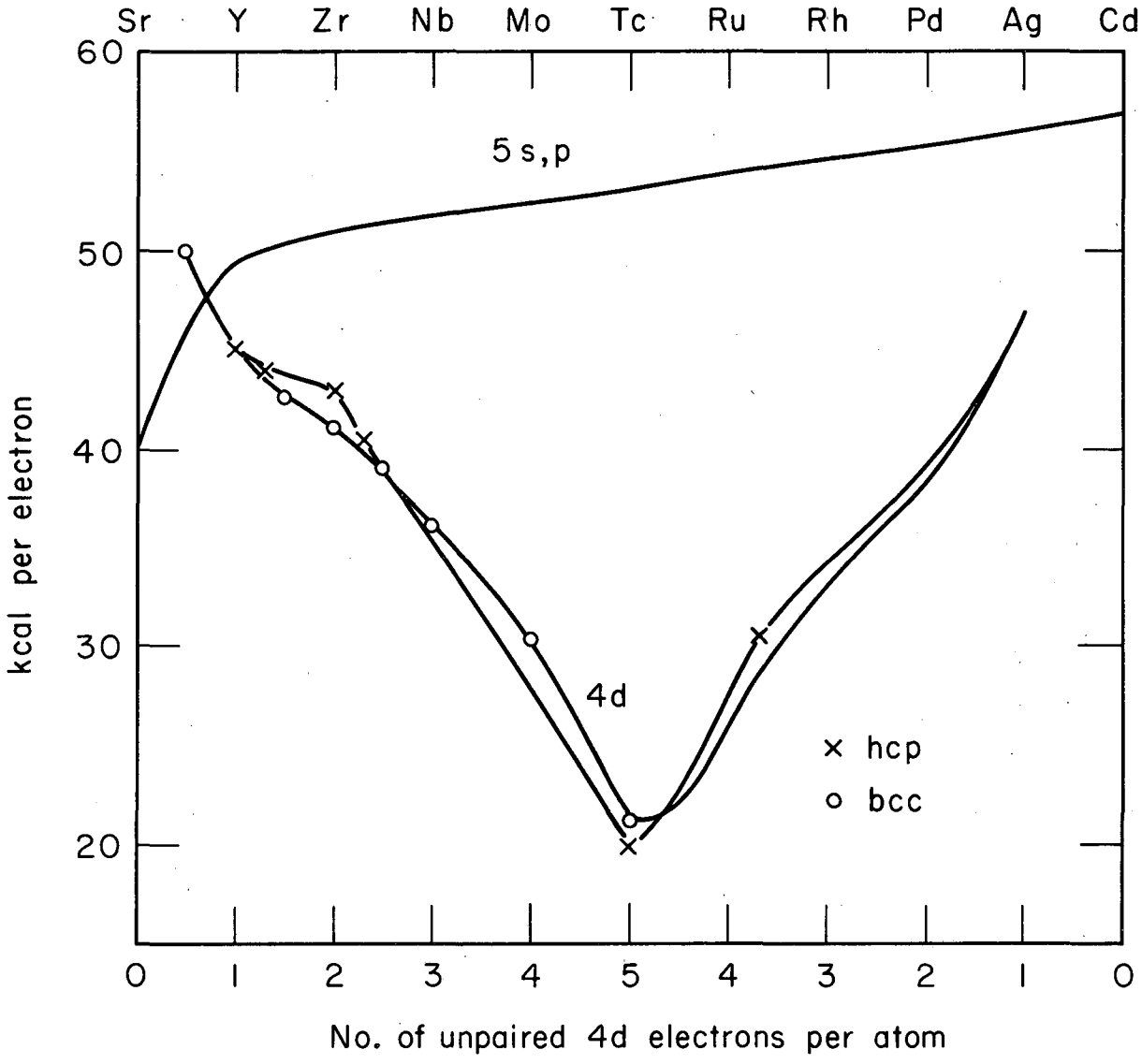


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Fig. 2

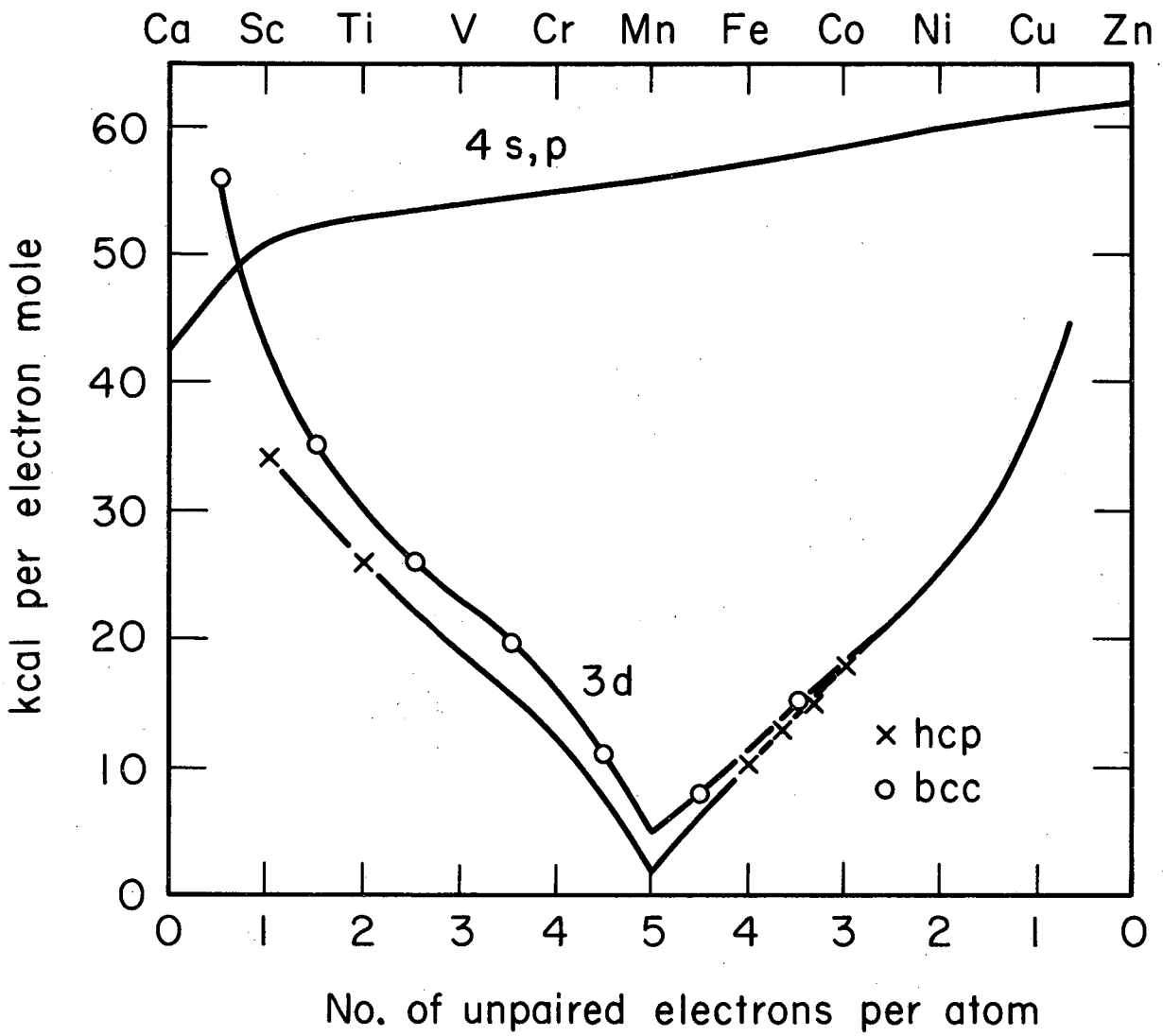

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Fig. 3

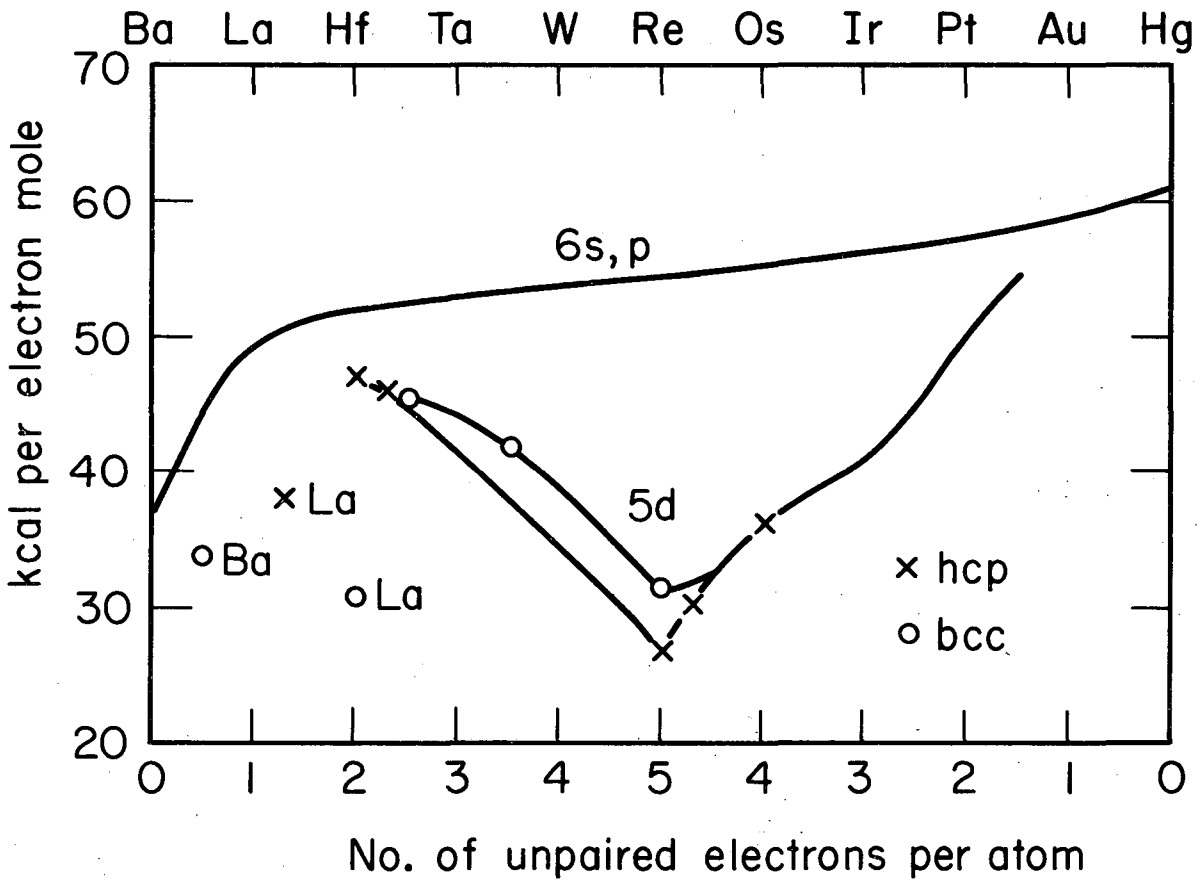

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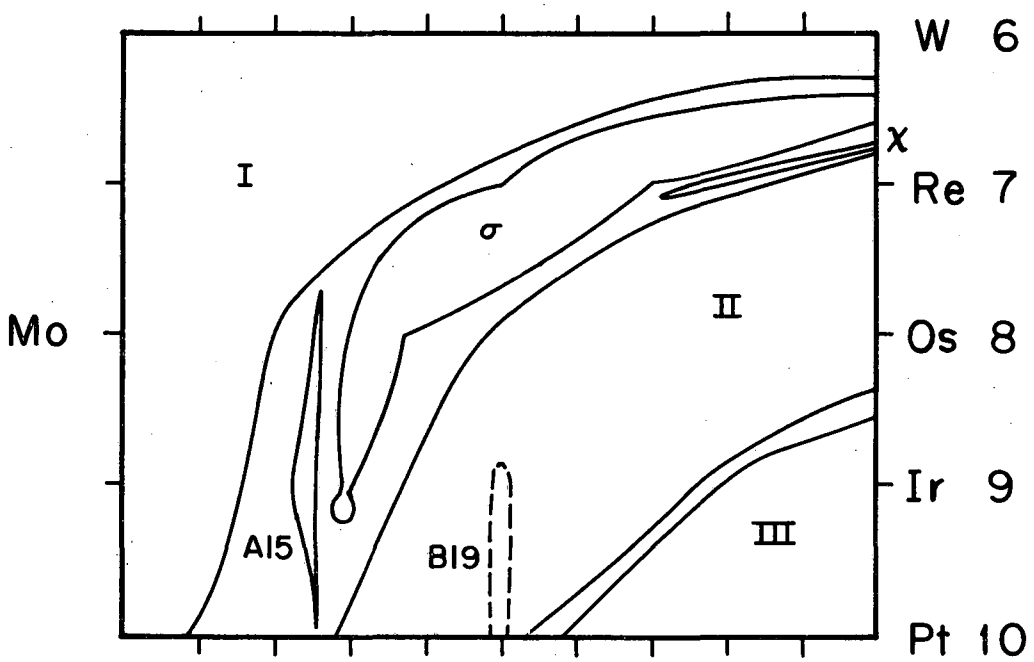
Fig. 4



MUB-2355-A

Fig. 5

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