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Author

Brewer, Leo.

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BONDING AND STRUCTURES OF TRANSITION METALS

Leo Brewer

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The great variety of structures and combining ratios in intermetallic compounds offers a challenge to bonding theories. Can the compositions and structures of these intermetallics be correlated and explained in terms of the same principles used for chemical substances generally?

For all substances it is the electrons through their interactions with the nuclei which constitute the glue that binds atoms together and any explanation of the structures, compositions and stabilities of intermetallic compounds must be based upon the same principles of electronic interactions that apply to all materials.

Valence-Bonds and Molecular-Orbitals

The common approaches to the description of electronic bonding are termed the molecular-orbital and valence-bond methods.¹ The molecular-orbital method starts with the atoms already assembled in the molecule or solid and then the electrons are added to molecular orbitals in an aufbau or building-up process patterned after the aufbau process for free atoms. The valence-bond approach starts with the electrons on the separated atoms, either in the ground electronic states or in low lying excited electronic states, and the bonding is described generally in terms of electron-pair bonds between the nuclei of the approaching atoms. It has been shown² that the methods become equivalent if used in full complexity. However, at a practical level of approximation, each method has serious deficiencies. The simple molecular-orbital method underestimates and the simple valence-bond method over-estimates electron-correlation due to the coulombic repulsion of the electrons in an electron-pair bond. The molecular-orbital method has the handicap of

breaking down for large internuclear distances, but it has the advantage of providing more readily information about excited electronic states of a molecule. Molecular-orbital theory has been extensively used in recent years for conjugated and aromatic molecules and has been the most common approach to metallic bonding through use of the electron-band model. However, the bulk of chemical bonding experience has been expressed in terms of the electron-pair bonding of the valence-bond model. Although the electrical and magnetic properties of metals, which are largely characterized by the density of electronic levels near the Fermi surface, are most satisfactorily described by molecular orbital approaches, it will be demonstrated in this paper that an extension of the valence-bond approach used by Pauling³ for metals as modified by Engel⁴ is the most practical way at present to apply the general background of chemical behavior of all materials to the understanding of the structures, composition ranges and thermodynamic stabilities of the phases of metallic systems.

Non-Metals

The application of the valence bond method to non-metals is familiar to most scientists. Thus chlorine atoms with the valence shell electronic configuration s^2p^5 form diatomic molecules with one electron-pair bond per atom, sulfur(s^2p^4) forms rings or linear chains with two electron-pair bonds per atom, while phosphorus(s^2p^3) forms three electron-pair bonds per atom in the tetrahedral P_4 molecule found in the gas and in white phosphorus or in the puckered graphite-like structure of black phosphorus. As a p orbital can accommodate only six electrons divided into two groups of opposing spins, it is seen that the structures as determined by the

number of electron-pair bonds per atom are fixed by the number of unpaired electrons in the free atom.

The ground electronic configuration of Si, s^2p^2 , has only two unpaired electrons, but the excited configuration sp^3 , with four unpaired electrons, is sufficiently close to the ground state so that the promotion energy⁵ of 95 kcal/gram atom required to unpair the two s electrons of the ground electronic configuration by excitation to the sp^3 configuration is smaller than the additional bonding energy due to the additional two electron-pair bonds which can be formed by the sp^3 configuration. Thus silicon forms the diamond structure with each atom bonded to four other atoms.

The common feature of the above examples was the correlation of molecular structure to electronic configuration because of the limitation of the number of bonds per atom to the number of unpaired electrons per atom. When, as for the fourth group elements, a relatively low lying electronic configuration, which has more unpaired electrons than the ground configuration, is available, the excited or promoted configuration will dominate the bonding and therefore the structural characteristics. For these four elements, from Cl to Si the atomization enthalpies, the enthalpy changes upon breaking the bonds of the solid to produce gaseous atoms, in the ground electronic state, are 32, 67, 80 and 109 kcal/gram atom, respectively.

Non-Transition Metals

The valence-bond theory can be applied in a similar manner to metals to determine the number of electron-pair bonds per atom. The principal difference between the metals and the non-metals is that the non-metallic

elements have made maximum use of their orbitals and have filled all eight positions in the s and p orbitals through the formation of localized electron-pair bonds. Metals do not have enough electrons to make full use of their s and p valence orbitals. The availability of vacant orbitals allows the electrons to resonate among all of the orbitals of adjoining atoms and to become somewhat delocalized; thus the characteristic metallic electrical conductivity occurs.

Sodium, magnesium, and aluminum, the metals of the third row of the periodic table, will be taken as examples. Sodium, with one 3s valence electron, can form only one electron-pair bond per atom, but this bond is spread out over the eight nearest neighbors and the six next nearest neighbors of the body-centered-cubic (bcc) structure and even farther. Magnesium, with the ground electronic configuration $3s^2$, would not be able to form any electron-pair bonds if it were not for the next excited configuration 3s3p. The promotion energy⁵ of 63 kcal/gram atom to excite the $3s^2$ configuration to 3s3p is small enough to be offset by the bonding energy of 98 kcal/gram atom provided by the two unpaired electrons of the 3s3p configuration; the two electron-pair bonds are spread among the twelve nearest neighbors and more distant neighbors of the hexagonal-close-packed (hcp) structure. For aluminum 83 kcal/gram atom must be used to promote the s^2p to the sp^2 configuration to make full use of its electrons and its three electron-pair bonds per atom are spread among the twelve nearest neighbors and more distant neighbors of the cubic-close-packed (ccp) structure. The atomization enthalpies for Na, Mg, Al and Si are 26, 35, 78 and 109 kcal/gram atom, respectively.

The three general principles that were illustrated in application of the valence-bond theory to the examples of both metallic and non-metallic elements of the third row of the periodic tables are: (1) the number of electron-pair bonds per atom due to a given electronic configuration of the element is determined by the number of unpaired electrons of the free atom, (2) low-lying electronic configurations with more unpaired electrons than the ground electronic configuration may predominate if the bonding energy from the additional electron-pair bonds offsets the promotion energy of the excited state, (3) each bonding electronic configuration produces a characteristic stable solid structure.

Transition Metals

For the fourth row or first long period of the periodic table, the metallic state does not end with the fourth valence electron at Ti but continues through the first transition series and only ends with the fourteenth valence electron at Ge. Examination of the spectroscopic data⁵ for the gaseous atoms indicates that the 3d orbitals are close in energy to the 4s and 4p orbitals. Until these 3d orbitals have been filled, it is not possible to fill up the s and p orbitals to achieve the sp^3 configuration which produces the non-metallic diamond structure.

Table 1 tabulates⁶ the crystal structures of the stable solid forms of the metallic elements to be discussed here. When an element undergoes transformation upon heating above room temperature, the lowest structure is the room temperature form with the order of structures given in order of occurrence with increasing temperature. The body-centered cubic (bcc) structure of the one-electron alkali metals is designated as structure I.

The hexagonal-close-packed (hcp) structure of Mg is designated as structure II. The cubic-close-packed (ccp) structure of Al is designated as structure III. This nomenclature has been chosen to emphasize the Engel correlation⁴ between the occurrence of these three structures and the presence of 1, 2, and 3 bonding electrons of the s,p type, respectively. In Table 1, it will be seen that the simple sequence of structures I, II and III that we observed for Na, Mg, and Al is more complicated for the transition metals, but we note that the (bcc) structure I is observed at least as the high temperature structure of all of the metals of the first six columns of the three transitions series. On going to the right, the (hcp) structure II is observed for metals of the seventh and eight columns of the second and third transitions series, and finally the (ccp) structure III is observed for all of the transition metals to the right. Although the data were less complete then, Engel⁴ suggested that this sequence could be understood if it were hypothesized that the structures were determined by the number of s,p electrons and that the (bcc) structure I of the alkali metals persisted until molybdenum and tungsten because of the d orbitals acting as a sink for the electrons beyond the one s electron until the d⁵s configuration is reached. Calculations⁷ have indicated that hybridization of d orbitals with s and p orbitals could produce results in agreement with the Engel correlation. A more definitive proof of the Engel correlation can be given from examination of the spectroscopic data⁵ for the gaseous atoms.

Qualitative Test of Engel Correlation

From analysis of the spectra of the transition elements of the first six groups, one finds⁵ that the low lying electronic configurations are of the type $d^{n-2}s^2$, $d^{n-1}s$, and $d^{n-2}sp$, where n is the total number of $(d+s+p)$ valence electrons, with d^n , $d^{n-1}p$, $d^{n-3}s^2p$ and $d^{n-3}sp^2$ somewhat higher in energy. For elements of the first six groups, $d^{n-1}s$ and $d^{n-2}sp$ are the lowest configurations with all of the electrons unpaired and available for bonding. Comparisons of promotion energies and bonding energies indicate that these two configurations should be the most important bonding configurations. For economy of space, these comparisons will be largely restricted to the metals of the second transition series, Rb to Ag, and the reader is referred to more detailed discussions^{6,8} for similar comparisons for the first and third transition series metals. Figure 1 illustrates the relative energies⁵ of these two configurations for the gaseous elements Sr to Mo of the second transition period. The energies of each configuration are presented as bands since there will be, in general, several spectroscopic states from each electronic configuration corresponding to different combinations of spin and orbital momenta of the electrons. Figure 1 shows the range of energies of spectroscopic states of highest spin multiplicity corresponding to each of the electronic configurations. In general, the d orbitals, which are in an inner shell, become stabilized with respect to the s and p orbitals of the outer shell as the nuclear charge increases from left to right in a transition metal period. For Sr, Y, and Zr the two configurations are close enough in energy that both configurations would be expected to be important and by the Engel correlation both structure I and II corresponding to

configurations $d^{n-1}s$ and $d^{n-2}sp$ would be expected. For Nb and Mo, the $d^{n-1}s$ configuration has become so much lower in energy than the $d^{n-2}sp$ configuration that one would expect the hcp structure II to be unstable. Both configurations have the same number of bonding electrons; so the large difference in promotion energy cannot be compensated by additional bonding energy as in the example of Mg where the excited sp configuration with two bonding electrons predominates over the s^2 configuration with no bonding electrons.

Reference to Table 1 shows that Nb and Mo have only the bcc structure I at all temperatures and also to the highest pressures available in agreement with the Engel correlation. For Sr, Y, and Zr, Table 1 indicates that the bcc structure I is stable at high temperatures and transforms to the hcp structure II at lower temperatures. Recent observations⁹ indicate that for Sr, small amounts of hydrogen may be necessary to stabilize the hcp structure, but the energies of the bcc and hcp phases must be very close. The greater lattice vibration of the bcc structure of lower coordination number produces a higher entropy which is the requirement for high temperature stability when two structures have comparable energies. The only exception to this general behavior is that of iron where differences in magnetic contributions to the entropy at lower temperature are greater than differences in vibrational contributions and allow bcc iron to transform to ccp for a short temperature interval before reverting back to the bcc structure at higher temperatures.¹⁰

Basis of the Engel Correlation

We have seen above that each non-metal has a structure clearly correlated with the total number of s,p valence electrons per atom. The

extension of this concept to metallic systems was first made by Hume-Rothery¹¹ who noted that many intermetallic compounds of greatly varying compositions had the same crystal structure if the average number of valence electrons per atom were the same. This very important concept of Hume-Rothery phases of characteristic structure associated with a limited range of electron per atom concentrations implies that a plot of excess free energy versus composition or versus valence electron concentration must turn up rather steeply at certain limiting electron concentration. From examination of alloy systems where the bonding is due to only s,p electrons, one can correlate the occurrence of ccp structure III with a range of approximately 2.5 to 3 s,p electrons per atom. For hcp structure II, the free energy appears to rise steeply beyond the limits 1.7-2.1 s,p electrons per atom and the bcc structure I is limited to a concentration of s,p electrons of less than 1.5 s,p electrons per atom. Other structures which also show characteristic electronic concentration limits will be discussed later. The transition metals have been stumbling blocks to the more general application of the Hume-Rothery rules because of uncertainty about the valence. The use of the total number of valence electrons including the d electrons did not yield consistent predictions.

The Engel correlation which uses only the s,p electrons in correlations between structure and electronic concentration now allows extension of the concept of Hume-Rothery compounds to the transition metals. Spectroscopic data have been used in the discussion above to confirm the Engel correlation qualitatively. A quantitative verification will be presented below. Why is the structure determined only by the s,p electrons and not by the d electrons? Of course the d electrons play

an important role in determining structure indirectly since relative stabilities of d electrons compared to s or p electrons in the gaseous atoms together with the energy resulting from electron-pair bonding of the unpaired electrons determines how many s,p electrons are available for bonding. The relative roles of the d and s,p electrons can be illustrated by the example of the condensation of gaseous tungsten atoms in their d^4s^2 ground state first to the liquid state. The calculations of the next section indicate that the promoted configuration, d^5s , with six electrons available for bonding predominates in the liquid with the five d electrons contributing over 150 kcal to the bonding energy while the contribution of the s electron is only 54 kcal. As the temperature is lowered to produce the solid, the major contributors to the cohesive energy, the localized d bonds, do not influence long-range structure, but the far-ranging s electron bonds do establish the body-centered cubic structure. Thus the Engel correlation implies that once the influence of d electrons in determining promotion energies and bonding energies has been considered, the crystal structure is fixed by the concentration of remaining s,p electrons. It has been noted above⁷ that a hybrid mixture of one s orbital with varying numbers of d orbitals could produce the bcc structure I and similar results are obtained for the relation between $d^{n-2}sp$ and hcp structure II. Another rationalization can be made on the basis of localization of the d electrons due to poor overlap of d orbitals. In contrast to transition metal ion complexes where s and p electrons are generally somewhat localized and thus can often form good hybrid bonds with d electrons, the s and p electrons in a metal are greatly

delocalized; they have become an electron gas. The d electrons, which belong to an inner electron shell, are much more localized and cannot obtain good overlap with s and p electrons. Bonding considerations to be discussed below indicate that the main d bonding contribution appears to come from d-d bonding. In terms of band theory, the d bands are somewhat separated from the s,p or metallic electron bands. If the d electrons are localized to bonds with only nearest neighbors, whereas the s,p electrons range far out into the metal, it is not unreasonable to assign the determination of long range structure to the s,p electron concentration.

The quantitative test of the Engel correlation for pure metals as well as the extension to alloy systems to be given below will be based on the occurrence of bcc structure I up to $sp^{0.5}$ or a maximum of 33% p character for the metallic or s,p electrons. Structure II will be associated with the range $sp^{0.7-1.1}$ or 41-52% p character for the metallic electrons. Structure III will be correlated with $sp^{1.5-2}$ or 60-67% p character for the metallic electrons. For contrast, the sp^3 configuration of the diamond structure has 75% p character.

It is not immediately obvious whether the number of s,p or metallic electrons per atom or the percent p character of the metallic electrons would be the decisive factor in determining long range structure. In the application of the Engel correlation, either could be used since almost all effectively-bonding electronic configurations have essentially one s electron per atom and there would be a one to one correspondence between the number of s,p electrons per atom and percent of p character of the metallic electrons. There is one situation where there would be a distinction. At the beginning of each period, the closed electronic

shells are rather expanded and polarizable. Upon moving to the right in the periodic table, the increasing nuclear charge rapidly causes a contraction of the shell and close-shell polarization effects should become negligible after the alkali and alkaline earth metal groups. Pauling³ estimated considerable p character in the alkali metal and diatomic molecules due to hybridization between s and p orbitals. Recent pseudopotential calculations¹² suggest that polarization of the closed electronic shell of sodium plays a significant role in the bonding and that there is considerable mixing of closed-core p electrons with the s valence electrons to increase the p character of the bonding electrons even more than considered by Pauling. Certain anomalous structure occurrences to be discussed below indicate that possibly the percent p character may be the controlling factor. However, this ambiguity exists only for the alkali and alkaline earth metals and can be ignored for the other transition metals. In the application of the Engel correlation, it will be the number of s,p electrons per atom that will be considered decisive.

Quantitative Application of Engel Correlation

- We can now use the Engel correlation in a more quantitative manner to allow prediction of the thermodynamic properties of bcc and hcp structures even when they are not observed for the pure element. For all of the transition metals except rhodium and palladium, atomic spectroscopy has yielded⁵ complete data on the relative energies of the $d^{n-1}s$, $d^{n-2}sp$ and $d^{n-2}s^2$ electronic configurations where n is the total number of valence electrons. The experimental¹³ heats of sublimation

of the metals given in Table 2 correspond to the ground electronic state of the gaseous atom, which is often the $d^{n-2}s^2$ state. The spectroscopic data allow calculation of the energy difference between the metallic state and the bonding valence states $d^{n-2}sp$ and $d^{n-1}s$, depending upon the structure. For example for Sc, 90 kcal/gram atom for atomization of the solid to $Sc(d^2s)$ and 45 kcal for promotion to $Sc(dsp)$ yields a valence state bonding energy of 135 kcal/gram atom. Table 3 shows the bonding energy⁸ of the $d^{n-2}sp$ valence state in the hcp structure or the energy required to vaporize the metal in the hcp structure to gaseous atoms in the $d^{n-2}sp$ state. It has been noted above that composition ranges for alloys show that each structure occurs over a finite range of electron concentrations. It is possible to calculate the minimum energy within each range to fix the effective electronic concentration as indicated in Table 3 and discussed in more detail elsewhere.⁸ Similar tables can be prepared for the bonding energy of the bcc structure from its valence state. This bonding energy is due in part to the bonding of s and p electrons on one hand and d electrons on the other hand.

Figure 2 has been prepared⁸ by estimating the variation due to increasing nuclear charge of the bonding energy per electron for s and p electrons between the known values for the group IIA and group IIB metals. The average value given by the 5 s,p curve is used for either s or p electrons. The s and p contributions have been subtracted from the total bonding energies such as tabulated in Table 3 to yield the resulting bonding energy per electron for the d electrons. The abscissa for the s,p electron bonding is the atomic number which is indicated above by the atomic symbol. The abscissa for the d electron bonding is the

number of unpaired d electrons available for bonding which runs from 0 to 5 and back to zero again. Data for both the bcc and hcp structure are given and it is seen that the bonding energy of a d electron decreases as more and more electron pair bonds are crowded around an atom with a minimum in the bonding energy per electron reached when five d electrons per atom are used for bonding. The data for both bcc and hcp structures follow closely the same smooth curve.

The characteristic variation of d electron bonding with number of d electrons is found⁸ also for the first and third transition periods. The major difference is the very pronounced increase in the bonding effectiveness of the d electron upon going down in the periodic table from the first to third transition series. This trend is opposite to the general decrease in s,p bonding effectiveness with increasing internuclear distances upon going down in the periodic table. For metals of the second and third transition series, the d-electrons can be used so effectively in electron-pair bonds that no electrons are left unpaired. Since unpaired d electrons are required for magnetism, the metals of the second and third transition series are not magnetic. For the metals Cr to Ni of the first transition series, the relative ineffectiveness of the d electron bonding with spin-pairing can be seen by comparing Fig. 3 with Fig. 2. For these metals the bonding energy that could be obtained by concentration of an electron pair between the nuclei is offset by the reduced coulombic repulsion between unpaired electrons. Thus some of the d electrons are left unpaired resulting in magnetism for these metals.

With the exception of Mn, all of the other thirty-two transition metals occur only with the bcc, hcp, or ccp crystal structures. The minor distortions or modifications of the hcp form that occur in a few instances can be neglected. How well do the observations fit the predictions of the Engel correlation? Spectroscopic data for the $d^{n-1}s$ and $d^{n-2}sp$ configurations, which are correlated to the bcc structure I and the hcp structure II, respectively, are sufficiently complete to allow predictions of the stabilities of these structures on a qualitative basis as outlined above in connection with the discussion of Fig. 1 or on a quantitative basis through comparison of bonding energies of d versus s,p electron pair bonds as given in Figs. 2 and 3 together with the spectroscopic promotion energies. For example, Table 4 summarizes⁸ the quantitative predictions by tabulating values for ΔH_{298}° of sublimation to the ground electronic state of the gaseous atom of the bcc and hcp forms of most of the transition metals. The values in parentheses are predicted values for structures which are not observed as stable phases. In all instances where the calculations of Table 4 based on spectroscopic data for the gaseous atoms and the Engel correlation between electronic configuration and crystal structure indicate that a structure is unstable by 2 kcal/gram atom or more, the experimental observations summarized in Table 1 confirm that the predicted unstable structure is not found to be stable at any temperature or at any pressure that has been used. There are eleven instances where the bcc and hcp structures have enthalpies within 1 kcal of each other. Sr, Y, and Zr have already been discussed above in connection with Fig. 1. For Sc, Ti, La, and Hf, where the bcc structure has a higher enthalpy than the hcp structure by 1 kcal, the hcp structure

is stable, but transforms to the bcc structure at higher temperatures because of the higher entropy of the bcc structure as discussed in connection with the high temperature stability of the bcc phase of Sr, Y, and Zr. For Ca, where the calculations indicate the same enthalpy for bcc and hcp structures, the hcp structure is unstable with respect to the bcc phase of higher entropy but can be stabilized by small additions of hydrogen.¹⁴ The calculations for Mn indicate that it occupies a unique situation in that all three electronic configurations yield comparable stabilities. As a result, Mn forms the complex α -Mn and β -Mn structures, designated as χ and β in Table 1, which are known for a number of binary and ternary systems with atoms of different sizes to meet the packing requirements of these structures for atoms of different size in different sites. Because of the availability of three electronic structures of comparable stability, manganese is able to provide the atoms of different size itself by assuming different electronic structures depending upon the crystal site. Uranium and plutonium appear to provide two additional examples of this type of behavior.

For Ni and Fe, the bcc structure is calculated to be more stable than the hcp structure by 1 kcal/gram atom. The hcp structure of Fe is unstable with respect to the bcc structure, but it is stabilized by 110 kilobars at 490°C. The bcc and hcp forms of Ni are calculated to be unstable with respect to the ccp form by 5 kcal and only the ccp structure is observed.

The spectroscopic data for the $d^{n-3}sp^2$ configuration are not complete enough for quantitative calculations of the enthalpies of the ccp phases. However, the sublimation heats of the ccp phases of Mn, Fe and the metals of the ninth, tenth, and eleventh groups are known. The comparison of these values with the calculated values for the bcc and hcp phases shows that the ccp phase is the only one observed when the calculated heats of sublimation of the bcc and hcp phases are smaller than the values for the ccp phase. For Mn, Fe, and Co, where several structures have closely the same enthalpy, one can say that the values are consistent with reasonable estimates of the $d^{n-3}sp^2$ promotion energies based on the observed energies required to promote d electrons to p electrons for other electronic configurations.

The bcc and ccp structures are found for Mn and Fe but not for Tc, Re, Ru, and Os, the corresponding group 7 and 8 metals of the second and third transition series. The calculations indicate that the higher energies required for promotion of d to p electrons for Tc, Re, Ru and Os are primarily responsible for the instability of the ccp structure. The bcc structure is unstable with respect to the hcp structure for the second and third transition series mainly because of the much higher bonding ability of the d electrons. A transformation from $hcp(d^{n-2}sp)$ to $bcc(d^{n-1}s)$ for metals of the seventh group or beyond would cause loss of two bonding electrons (one d and one p).

The stability of the ccp structure for the ninth, tenth, and eleventh groups is consistent with the Engel correlation since the bonding energies shown in Fig. 2 indicate that the expected d to p promotion energies are more than offset by the additional d and p electron-pair bonds to yield bonding states with promotion at least to $d^{n-2.5}sp^{1.5}$. For example, the

promotion of 2 d electrons per atom from $Au(d^{10}s)$ to $Au(d^8sp^2)$ would increase the number of electrons available for electron-pair bonding from one to five electrons per atom. All of these electrons would be spin-paired in the formation of electron-pair bonds; the d orbitals would be completely occupied. Likewise, the s and p electrons would be spin-paired in the usual manner of metallic s, p electrons.

For the metals of the fourth to sixth groups, even the rough estimates of the promotion energies of the $d^{n-3}sp^2$ configuration together with bonding energies calculated from plots such as those of Figs. 2 and 3 are sufficient to clearly predict instability of the ccp structure for these metals. Accurate spectroscopic data are available for Y which predict that ccp Y is unstable by 20 kcal/gram atom relative to hcp or bcc Y. The spectroscopic data for Sc and La are too incomplete for accurate calculations of the thermodynamics of ccp Sc and La.

The explanation for the increase of bonding strength of d electrons from the first to third periods given above in terms of poor overlap of 3d orbitals is an important concept for predicting the stabilities of intermetallic compounds. For example, metals of the first transition series with poor d orbital overlap are greatly stabilized in structures, such as the Al_5 or V_3Si structure, which tend to squeeze the atoms abnormally closely. Likewise the effect of compression through application of external pressure can be predicted on the basis that compression improves the bonding ability of the poorly overlapping d orbitals more strongly than for the s or p orbitals. Thus one would predict that application of pressure would stabilize the structure with the greatest number of bonding d electrons relative to other structures. For the transition metals of the first six groups, the bcc structure with $d^{n-1}s$

configuration has the most bonding d electrons according to the Engel correlation and would be predicted to be stabilized by pressure with respect to the hcp or ccp structures even though these close-packed structures have higher coordination numbers. This requires that the bcc structure for the first six groups be more dense or at least more compressible and therefore more dense under pressure than the close-packed structures. The data for Ti, Zr and Hf are in agreement.¹⁵ On this same basis, one can predict that the close-packed structures of the fifth and sixth group metals will not be stabilized by pressure. For transition metals beyond the sixth group, the $d^{n-1}s$ configuration will have fewer bonding d electrons than the hcp or ccp configurations which correspond to promotion of paired d electrons to unpaired p electrons. Thus pressure should favor the hcp structure over the bcc structure beyond the sixth group and should favor the ccp structure over the hcp structure beyond the seventh group. High pressure data are fragmentary, but the available data¹⁵ are largely in agreement with the predictions based on the Engel correlation.

Contradictions to Engel Correlation

Of the ninety-nine possible predictions for the three structures of the thirty-three metals of the three transition series of the periodic table, the only two clear contradictions are the occurrence^{9,14} of ccp phases at low temperature for Ca and Sr. The Engel correlation would require at least 2.5 s,p bonding electrons per atom with at least 60% p character. Going outside the group of thirty-three transition metals, a few additional exceptions are known. For example, the occurrence¹⁶

of hcp phases of Li and Na at very low temperatures would require at least 1.7 s,p electrons per atom with at least 41% p character to be consistent with the Engel correlation. It has been suggested⁷ that these anomalous occurrences are related to the anomalous order of stability for the rare gas structures. The discussion above in the section headed Basis of the Engel Correlation has indicated that polarization of the closed electronic cores of the alkali and alkaline earth metals to increase the p character of the valence electrons may be the significant factor responsible for the anomalies. Whether this is the correct explanation or not, the anomalous structures are only found with weakly bonded materials near the beginning of a period and the factor responsible need not be considered for the remainder of the metals.

Multicomponent Phase Diagrams

As for the pure metal, the electronic configurations are the primary factors that fix the thermodynamic and structural properties of inter-metallic phases. However, it is necessary also to consider the effect of size differences of the component atoms, internal pressure differences, and charge transfer.

In structures with all lattice sites equivalent, the mixing of atoms of different sizes tends to reduce thermodynamic stability. On the other hand, there are a number of structures, characteristic of intermetallic phases such as the α -Mn (or χ), the β -Mn, and the β -U (or σ) structures for which different volumes are available at different crystal sites and a mixture of atoms of different sizes is required for maximum stability.

The internal pressure, which is commonly evaluated from the quotient of the molal energy of vaporization divided by the molal volume, is a measure of the interatomic attractive forces. Internal pressures have been successfully applied through the regular solution theory¹⁷ to the prediction of solubilities and other thermodynamic properties for many types of solutions. The application of size and internal pressure factors to transition metal systems is discussed in detail elsewhere⁶ and the present discussion will be limited to the effects of electronic configurations and charge transfer.

It has been mentioned earlier that the Hume-Rothery rules imply that the free energy of a bcc phase, for example, rises sharply beyond a limiting electron per atom concentration. For the bcc structure, this limit is around 1.5 electrons per atom for non-transition metals. Engel⁴ has extended the Hume-Rothery rules to transition metals by noting that the same rules are applicable to both types of metals if d electrons are not included in the electron per atom count. A considerable number of "electron" phases have now been characterized as being restricted to a limited range of s,p electrons per atom.

Fig. 4 will be used to illustrate the behavior of electron-phases. The complete diagram, including temperature as a variable, would require a six-dimensional plot. Fig. 4 represents a projection to a two-dimensional diagram.⁶ Each point corresponds to an alloy composition with the abscissa giving the atomic percent of molybdenum and the ordinate shown on the right hand side corresponding to the proportions of the right-hand metals given in terms of their average electron per atom contributions, varying from 6 for W to 10 for Pt. For example, a horizontal line at the Os

position (8 electrons per atom) 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 or bcc phase region extends from pure Mo to 20 a/o (atomic percent) Os, the Al₅ or Cr₃Si structure has a narrow composition range around Mo₃Os, the σ phase extends from 30 to 37 a/o Os, and the area labelled II corresponds to the hcp phase region from 48 to 100 a/o Os. The areas between the indicated phase regions correspond to two phase mixtures. A dotted area labelled B19 is an ordered phase region of AuCd structure which separates from the hcp phase at low temperature. A horizontal line drawn halfway between Re and Os would intersect the sequence of phase regions resulting from adding Mo to an equimolal mixture of Re and Os or an equimolal mixture of W, Re, Os and Ir. The elements on the right-hand side have been chosen from 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. If W, Re, Os, Ir, and Pt are mixed in varying proportions to yield an average valence electron concentration of 7.5 e/a, then the alloy behavior upon adding Mo to this mixture is predicted to be closely the same as indicated by the horizontal line midway between Re and Os. This type of plot which emphasizes the primary role of average electron concentration represents a maximum of information that can be presented in two dimensions and is closely in agreement with all the reliable data available.

It is of particular interest to note that as the average electron concentration is increased by adding fcc Ir or Pt to bcc Mo, a wide

region of hcp structure II is found to parallel the sequence I, II, III shown in Table 1 as the electron concentration in pure metals is increased from that of Mo and W to that of Rh and Ir.

If lines of equal electron concentration per atom were plotted across the diagram, they would be curved lines sloping, for example, from pure Re(7 e/a) on the right to a 25% Pt, 75% Mo alloy on the left. It will be seen the electron-phases such as structures σ , χ , I, II and III have boundaries which tend along isoelectronic lines. As indicated earlier, this must be due to a rapid increase in free energy at limiting electron concentrations. The actual phase limit will then be determined by thermodynamic considerations which must take into account the temperature, the thermodynamic activities in the saturating phase, and the other necessary thermodynamic criteria as has been discussed in detail elsewhere.⁶ Phase guides of the type of Fig. 4 not only condense a large amount of information into compact form, but they serve as guides to the prediction of phase diagrams which have not yet been studied. The need for such predictive ability is emphasized by the physical impossibility of experimental determination of the over two billion multicomponent phase diagrams resulting from combinations of only thirty metals. Plots like that of Fig. 4 together with the tables and text of Reference 6 provide reliable predictions of over one billion of the multicomponent phase diagrams of the transition metals.

Although it is the s and p electrons that determine the long range structure according to the Engel theory,^{4,6,8} the d electrons through their short range bonding play a decisive role in determining stability.

The discussion of the pure metals has emphasized that the metals of the left hand side of the transition series use all of their valence electrons in bonding, but they do have vacant d and p orbitals that are unused. On the right side, the transition metals use all of their d orbitals, but the internal pairing required by the Pauli principle makes some of the d electrons unavailable for bonding. On this basis, one would predict that an alloy of Zr and Pt, for example, should be unusually stable. One would expect transfer of d electrons from $\text{Pt}(d^7sp^2)$ to low-lying vacant orbitals of Zr. For every electron transferred with resulting unpairing of two internally-paired electrons, two electrons are made available for bonding by pairing between atoms. This prediction has now been confirmed by the demonstration that carbides of the metals of the left hand side of the second and third transition series, which are the most stable carbides known, are decomposed by platinum group metals to produce compounds such as ZrPt_3 with heats of formation ranging possibly up to 80 kcal/mole.¹⁸

A particularly simple illustration of the role of d electrons is the effect of small additions of transition metal solutes upon the equilibrium between the bcc and hcp phases of the fourth group transition metals. Any transition metal with three or more unpaired d electrons would not be able to make as good use of these electrons in bonding when surrounded by d^2sp Zr atoms (hcp II) as when surrounded by d^3s Zr atoms (bcc I). In confirmation, all transition metals, to the right of the fourth group with no known exception, stabilize the bcc phases of Ti, Zr, and Hf relative to the hcp phases.

The above illustrations point out the importance of applying the Engel correlation to obtain the distribution of valence electrons between d and s,p.

In addition to unifying the Hume-Rothery Rules and related rules for electron-compounds as applied to either alloys of only non-transition metals or of only transition metals, the value of the Engel correlation can be particularly shown by systems containing both types of metals.⁸

Summary

The same chemical bonding principles that have been applied to non-metals and compounds generally can be applied to metals including the transition metals. The Engel correlation between electronic configurations and crystal structures of metals has been combined with spectroscopic data for the gaseous transition metal atoms to calculate thermodynamic properties of the different crystalline forms of the transition metals, both stable and metastable. Recognition of the relatively poor overlap of bonding d orbitals allows prediction of the effect of pressure upon relative stabilities of different crystal structures of the transition metals and also leads to understanding of the limited occurrence of ferromagnetism among the transition metals. The concept of "Hume-Rothery phases" or "electron compounds" can be applied to transition and non-transition metals in a unified manner. The above procedures have been used to predict the crystal structures and maximum composition ranges of the intermediate phases of over one billion of the multicomponent phase diagrams of the transition metals.

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TABLE 1
Crystal Structures of Metals^a

Na	Mg	Al									
I	II	III									
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I	I III	I II	I II	I	I	I III β χ	I III I	III II	III	III	II
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
I	I II III	I II	I II	I	I	II	II	III	III	III	II
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	
I	I	I III II	I II	I	I	II	II	III	III	III	

^aI: Body centered cubic, A2. II: Hexagonal close packed, A3.

III: Cubic close packed, A1. χ and β are α -Mn and β -Mn structures.

The structures are listed in order of temperature stability with the room temperature structure lowest.

Table 2. Heat of atomization of solid elements¹³ in
kilocalories/gram atom at 293.15°K or at the melting
point, whichever temperature is lower.

Na	Mg	Al											Si	P	S	Cl	Ar
25.9	35	78											109	80 ±10	66	32.2	1.85
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
21.5	42.5	90	112	123	95	68	99.3	102.4	102.8	81.1	31.2	66	89.5	72 ±3	54	28.1	2.57
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
19.5	39	101.5	145.5	172	157	158	153	133	91	68.4	26.7	58	72	63	48	25.5	3.57
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po		
18.7	42.5	103	148	187	203	187	188	160	135	88	15.3	44	47	49.5	34.5		

TABLE 3
Bonding Energies of the $d^{n-2}sp$ Valence State in the Hexagonal Close-Packed Structure^a

Number of Bonding Electrons Per Atom											
2	3	4	5	6	7	6	5	4	2.4	2	
<u>In kcal/gram atom</u>											
Mg											
98											
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu*	Zn	
(84)	135	157	(165)	(158)	(120)	153	169	(171)	(135)	124	
Sr	Y	Zr	Nb*	Mo*	Tc		Ru*	Rh*	Pd*	Ag*	Cd
80	144	188	(197)	(198)	205		204	(189)	(165)	(130)	144
Ba	La	Hf	Ta	W	Re	Os	Ir	Pt		Au*	Hg
(74)	141	199	(230)	(244)	241	255	(234)	(215)		(140)	(123)

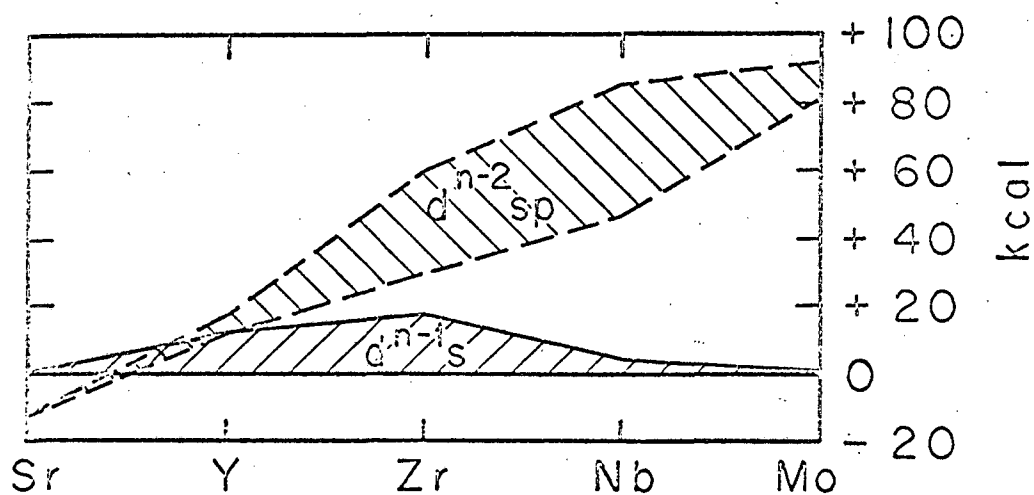
^a Asterisks indicate that bonding energy is given for the $d^{n-1.7}sp^{0.7}$ valence state. The number of bonding electrons per atom for Ru*, Rh*, and Pd* are, respectively, 5.4, 4.4, and 3.4. For Cu*, Ag*, and Au*, the $d^{9.3}sp^{0.7}$ valence state has 2.4 bonding electrons per atom. The method of calculating non-integral electronic configurations corresponding to the minimum energy is given in Reference 8.

TABLE 4

 ΔH°_{298} of Sublimation of BCC and HCP Phases of the Transition Metals^a

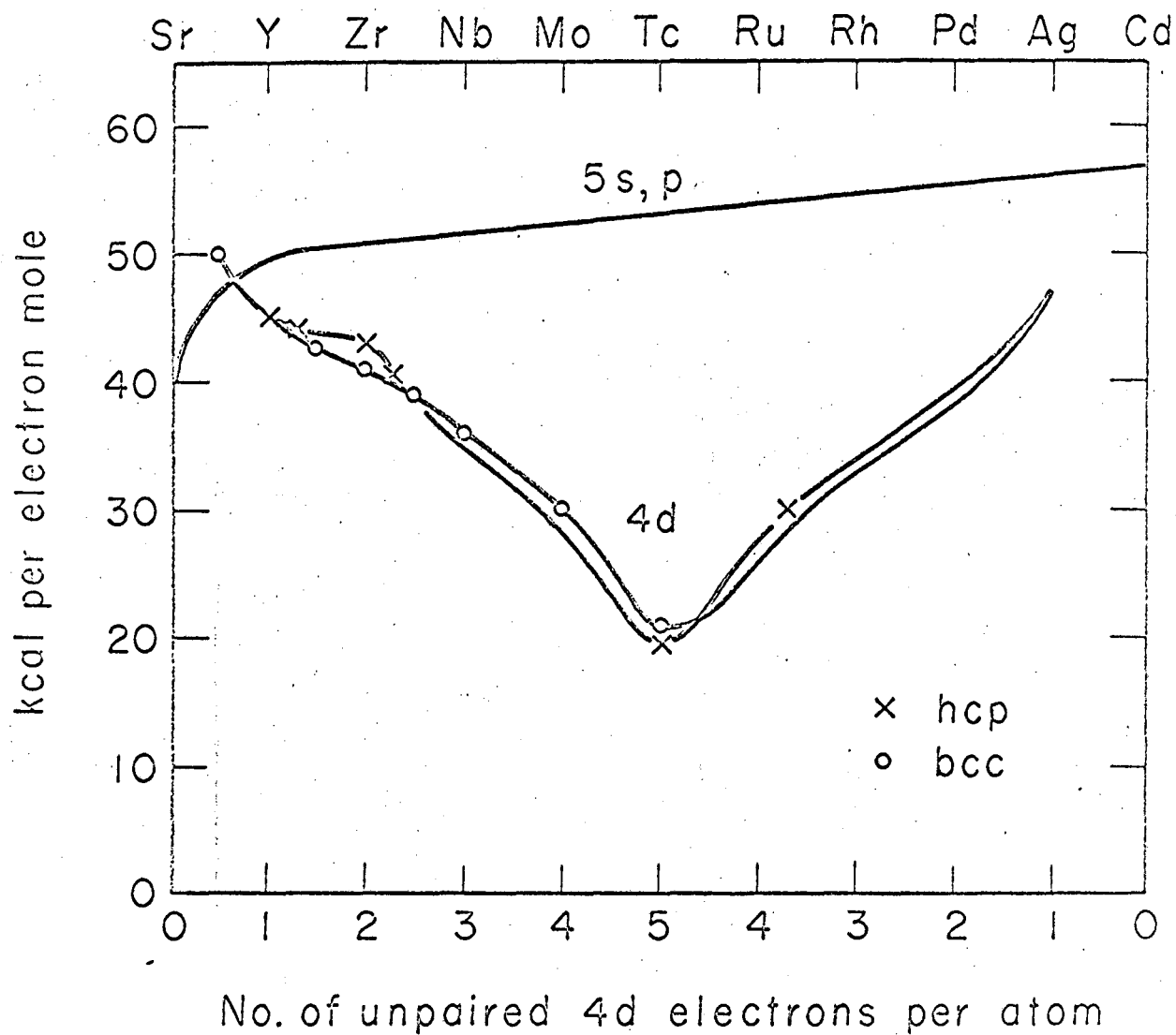
In kcal per gram atom										
	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
BCC	41	89	112	123	95	68	99	(100)	(98)	(61)
HCP	(41)	90	113	(118)	(87)	(68)	(98)	102	(97)	(56)
	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
BCC	38	101	145	173	157	(152)	(151)	(131)	(83)	(56)
HCP	39	102	146	(163)	(142)	158	153			
	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au
BCC	43	102	147	187	203	(184)	(177)	(155)	(124)	(59)
HCP	(41)	103	148	(181)	(189)	187	188	(159)	(129)	(55)

^a Values in parentheses are predicted values for unstable structures.



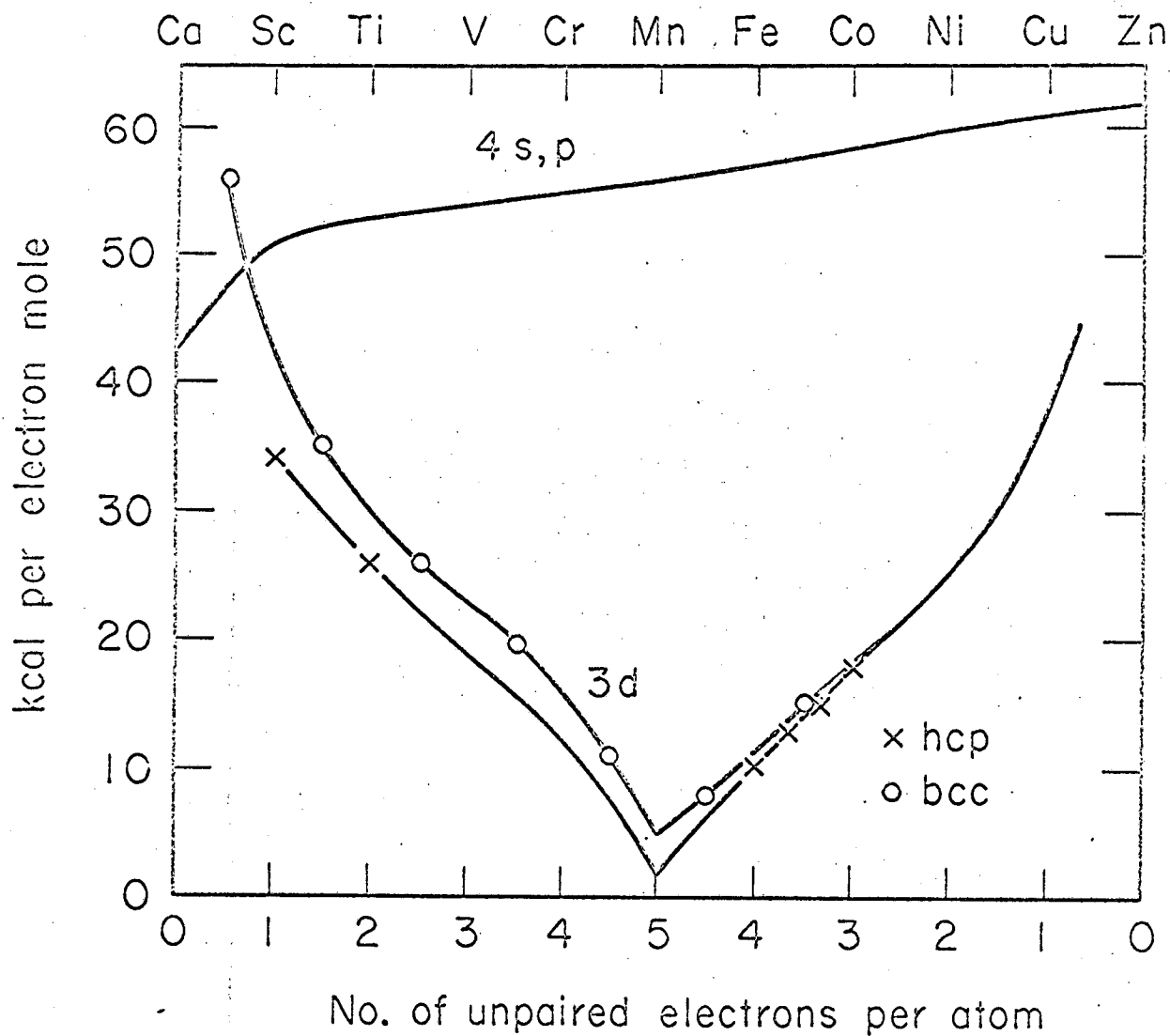
MUB-8895

Figure 1. Relative energies of the $d^{n-1}s$ and $d^{n-2}sp$ electronic configurations for gaseous atoms of the second transition series, kcal/gram atom.



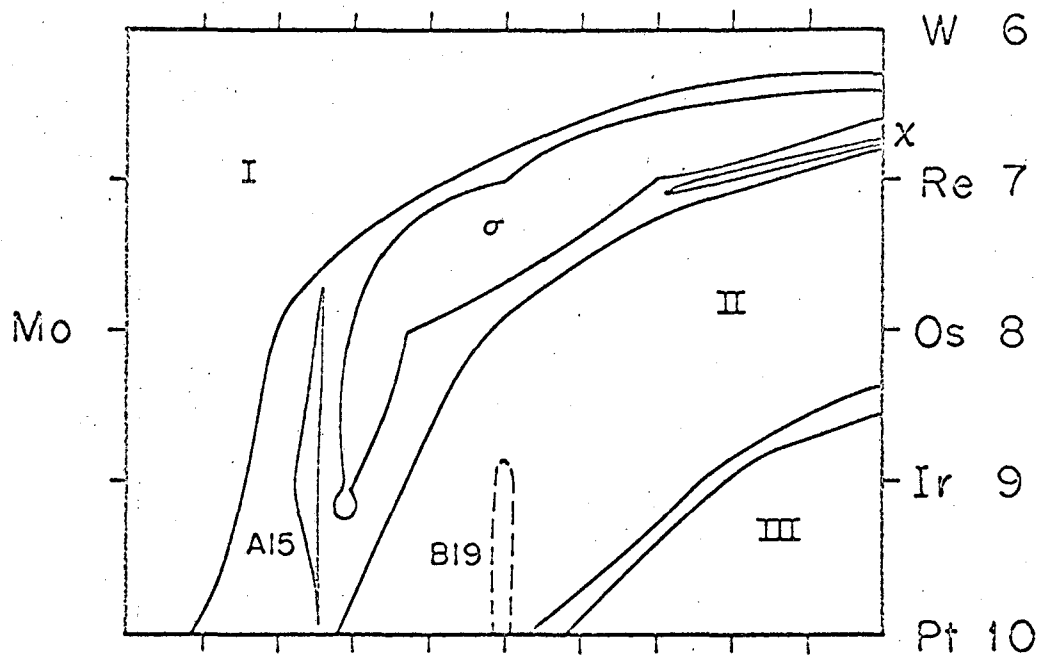
XBL6711-3829

Figure 2. Valence-state bonding enthalpy per unpaired electron in kcal/gram atom. Top Curve: Bonding enthalpy of 5s or 5p electrons versus element. Bottom Curve: Bonding enthalpy of 4d electrons versus number of unpaired d electrons.



MUB-9501

Figure 3. Valence-state bonding enthalpy per unpaired electron in kcal/gram atom. Top Curve: Bonding enthalpy of 4s or 4p electrons versus element. Bottom Curve: Bonding enthalpy of 3d electrons versus number of unpaired d electrons.



MUB-2355-A

Figure 4. Multicomponent phase diagram of Mo with third transition-series metals, projected along the temperature axis. Abscissa gives atomic percent of Mo in alloys.

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