Title

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Publication Date

1972-12-01

Presented at the Eighteenth Annual Conference
on Magnetism and Magnetic Materials
Denver, Colorado, Nov. 28, 1972

LBL-1424
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November 1972

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

TRANSITION METAL ALLOYS - A CHEMIST'S VIEW

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ABSTRACT

The valence-bond model, so widely used in chemistry, is equally applicable to transition metal alloys. In contrast to models commonly used by physicists, this model emphasizes the distribution of electrons in real space and the differences in spatial distribution of f and d electrons in contrast to s and p electrons. From the energies of the different electronic configurations that are known for almost all of the gaseous atoms and bonding energies for different types of electrons, one can calculate the energies of the electronic configurations in the metal. Thus Ba, Ta, and W with gaseous ground states s^2, d^3s^2, and d^4s^2 are calculated to have the predominant configurations ds, d^4s, and d^5s, respectively, in the metal.

The determination of the correct electronic configuration in the metal is the keystone to reliable predictions. The bonding energies due to the different types of electrons can be used to readily evaluate thermodynamic data to predict the stable composition range for a given structure, or the crystal structure that is stable at a given composition and temperature, and the effect of pressure, temperature and alloying upon the relative stabilities of different structures as well as the occurrence of magnetism.

INTRODUCTION

It has been suggested by some psychologists that the act of making a choice of a career is a selective force that tends to segregate scientists into groups with distinctly different ways of thinking about problems. If such different ways of thinking exist, one might argue whether psychological selection factors or differences in traditional ways of education in the various disciplines are the more important factors, but the need to schedule papers contrasting the views of chemists and physicists would seem to confirm that real differences do exist.

Let me briefly review what I think are some of the main characteristics of the chemist's way of thinking about materials in general. One of the features is the use of a variety of models. In setting up any model, one must reach some compromise between the degree of generality of the model and the ease of its employment for specific applications. The chemist, who generally uses these models to make on the spot predictions in the course of his everyday work in the laboratory, tends to favor models that are easy to apply to quickly yield reliable predictions even though their scope of application is limited and several different models must be used to cover a wide range of materials or properties. Thus a chemist talks about models based on ionic bonding, covalent bonding, van der Waals bonding, etc., and the training of a chemist involves not only knowing how to use the variety of models, but also the limits of these models and when not to use them. A simple illustration might be the use of valence-bond and molecular-orbital models to describe the properties of gaseous diatomic molecules. These models can be sufficiently elaborated to become essentially equivalent,[1] but they become impractically complicated. The simple forms of these models that are commonly used are, in some respects, contradictory. For example, the simple valence-bond model does not correctly predict the magnetic behavior of oxygen while the molecular orbital does, but the molecular orbital model is not as reliable as the valence-bond model in predicting bonding energies. Thus part of the difference between chemists and physicists is probably due to the chemist's need to be able to reliably predict detailed data quickly.

My introduction to the properties of transition metal alloys has been through the telephone calls I get from metallurgists and physicists at Berkeley and elsewhere, who expect a chemist to be able to answer questions such as "What will be the crystal structure of Mo_6Pt_4 at 1000 K?", "What compositions in the Mo-Os system will have the β-U crystal structure?", "Will increased pressure favor the body-centered cubic (bcc) or hexagonal close-packed (hcp) structure of Hf?", "Will the alloy $HfPd_4$ be stable in contact with graphite?", "Which alloy additions will stabilize the bcc structure of Hf?", etc. To be able to answer such questions on the telephone, it is necessary to have a model that will reliably yield predictions at least on a semi-quantitative basis within the few minutes available on the telephone. When thermodynamic predictions are desired to determine the range of compositions of a given structure or which crystal structure would be stable for a given composition and temperature, the valence bond model that has been so widely used for organic and inorganic compounds is equally applicable to transition metal alloys and is unexcelled for reliable predictions that can be quickly obtained with rather simple calculations. In contrast to models commonly used by physicists, the valence bond model emphasizes the distribution of electrons in real space and the difference in spatial distribution of f and d electrons in contrast to s and p electrons and the differences in their bonding energies.

BONDING OF VALENCE ELECTRONS

The properties of materials depend upon the interaction of the nuclei and electrons of the atoms in the materials. When the atoms have many electrons, the interactions become extremely complex. However, a large part of these complex interactions have already been characterized experimentally for the free gaseous atom through study of the optical spectra. The energies of most energy levels of an atom that lie low enough to play a role in the bonding of the atoms are accurately known. The valence-bond model takes advantage of this information by describing the bonding in the condensed phase in terms of interactions between the atoms in the gas as their internuclear distances are decreased. You are all familiar with the valence-bond model, but let me review some of the main features. In the valence-bond model, the cohesion of the condensed phases is ascribed to electrons that are able to act jointly on two or more nuclei. From quantum mechanics, we know that electrons cannot take all possible distributions in space around the nuclei. The spatial distributions of the electrons can be described in terms of orbitals which have characteristic distributions around the gaseous atom depending upon the main electronic shell and the orbital angular momentum. The Pauli exclusion principle plays an important role in determining whether electrons can contribute to the cohesive energy. The repulsion of the electrons in the filled 2s and 2p shells of Ar prevents concentration of these electrons at an intermediate distance between the nuclei in condensed argon thus preventing the bonding associated with electrons interacting strongly with both nuclei. On the other hand, for Cl atoms with one p orbital half filled, the Pauli exclusion principle does not prevent pairs of 2p electrons from concentrating between the Cl atoms and attracting both nuclei. Thus vacant orbitals that allow electrons to be shared between atoms are an essential feature of the bonding described by the valence-bond model. The enthalpy required to abstract a chlorine atom from solid chlorine, 32 kcal/gram-atom, is ascribed to the overlap of the half-filled 2p orbitals to allow one electron from each atom to interact with the nucleus of the adjoining atom. For sulfur, the element to the left of chlorine in the periodic table, two of the 2p orbitals are half-filled and two electrons from each atom can participate in bonding and the enthalpy required to abstract an atom from the solid is 66 kcal/gram-atom. If one goes down in the periodic table to Br and Se, the corresponding atomization enthalpies are 28 and 55 kcal/gram-atom, respectively. The reduced values are attributed to the larger radii of the filled electron shells, thus keeping the bonding electrons at a greater distance from the nuclei. The bonding enthalpies to be expected for one, two, three, or four bonding electrons per atom for s or p electrons of the seven main shells are well established and can be predicted with reasonable confidence where such bonding enthalpies are not experimentally available.

METALLIC ELECTRONIC CONFIGURATIONS

The gaseous atom is an assemblage of electronic states that interact as the atoms approach one another. Because the number of unfilled orbitals varies with electronic configuration, the vaporization of an atom from the condensed phase to the gas may result in a change in electronic configuration. For example, the ground-electronic state of Si is a ^3P state corresponding to the valence-electron configuration p^2s^2. However, because of the filled s orbital, only the two p electrons are available for bonding. The excited ^5S state corresponding to the configuration p^3s has four half-filled orbitals and four ele-trons available for bonding. Thus when Si atoms are brought together, the energy of states of the p^3s configuration drops more rapidly than that of the p^2s^2 configuration and solid silicon corresponds to bonding of Si atoms in the p^3s configuration with four electrons per atom contributing to the bonding. The net enthalpy of sublimation of solid silicon is thus the cohesive enthalpy of the p^3s ^5S state minus the energy difference between the ^5S and ^3P states, the promotion energy of the ^5S state relative to the ground ^3P state.

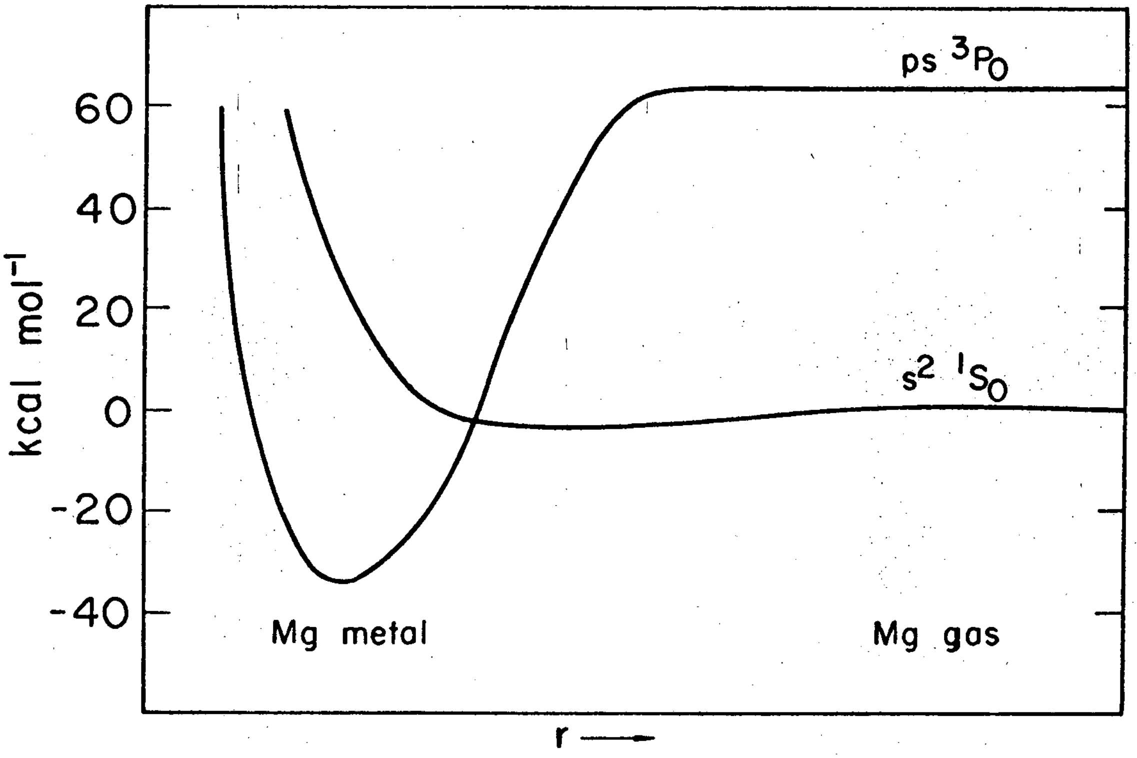

Figure 1. Energies of s^2 and ps configurations of Mg as function of internuclear distance.

The model is applied to metals or non-metals in the same manner. Figure 1 illustrates schematically the application to Mg for which atoms in the ground s^2 ^1S state can interact only weakly by the same van der Waals interaction responsible for cohesion of the noble gases since the Pauli exclusion principle does not allow overlap of the 3s orbitals and the s electrons cannot interact strongly with nuclei of adjoining Mg atoms. The magnitude of the van der Waals interaction between Mg atoms is known[18,19] from the potential energy curve of Mg_2. However, the excited ps ^3P state can interact strongly as the atoms approach one another with two electrons used for bonding. As the internuclear distance, r, is reduced the energy of states of the sp configuration falls below that of the s^2 configuration and the cohesion of Mg metal is due to two bonding electrons per atom. The net enthalpy of sublimation is the bonding enthalpy[2] of Mg atoms in the ps configuration of 98 kcal due to the two electrons minus the promotion energy of 63 kcal for the ps ^3P state of Mg.

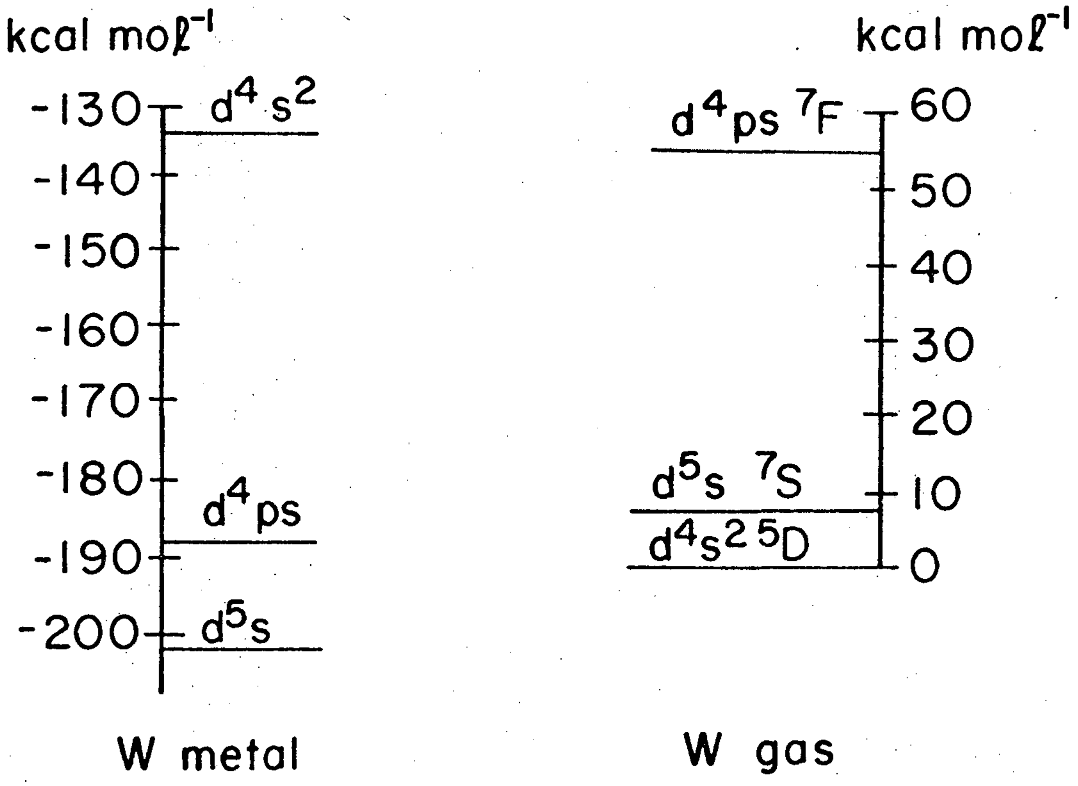

Figure 2. Energies of d^4s^2, d^5s, and d^4ps configurations of W for metallic internuclear distance and for the isolated atom.

Figure 2 illustrates the promotion energies of the d^4ps and d^5s configurations of tungsten relative to the ground d^4s^2 configuration for the isolated atom and the relative energies of the three configurations after the gaseous atoms have been brought together to the equilibrium distance in the solid. Bonding enthalpies associated with bonding electrons of the various main shells, which have been tabulated,[2] can be used to calculate that the bonding due to the four unpaired electrons of the ground state results in a bonding enthalpy of 136 kcal/gram-atom while the five unpaired d electrons and one unpaired s electron achieve a bonding enthalpy of

211 kcal/gram-atom. The d^4ps configuration has the highest bonding enthalpy of 243 kcal/gram-atom, but it is so highly excited in the free atom that metallic d^4ps tungsten is still 15 kcal/gram-atom above the d^5s configuration. Thus one calculates that the d^5s configuration is the predominant electronic configuration in tungsten metal even though it is not the gaseous ground state configuration. Similarly, Ta with a gaseous ground state d^3s^2 is calculated to be d^4s in the metal. Ba, like Mg, has a gaseous ground state s^2, but Ba metal is calculated to have the configuration 5d6s in the metal in contrast to 3p3s for Mg metal. As will be noted below, the change in crystal structure from hcp for Mg to bcc for Ba is attributed to this difference in electronic configuration.

The determination of the correct electronic configuration in the metal is the keystone to reliable prediction of metallic behavior. Calculations of this type to determine the predominant electronic configuration in the solid have been done for each of the transition metals.[2] For most transition metals, the ground state configuration for the gas is the $d^{n-2}s^2$ configuration where n is the total number of valence electrons. Due to the unavailability of the electrons in the closed s^2 orbital for bonding, the ground state $d^{n-2}s^2$ configurations do not drop in energy as much as $d^{n-1}s$, $d^{n-2}ps$, or $d^{n-3}p^2s$ configurations when the atoms are condensed, and the gaseous ground state configuration $d^{n-2}s^2$ is not important for the condensed metal. All of the configurations that are found to be important in the condensed metal have one s electron because of the non-bonding character of the s^2 configuration and the major factor that characterizes the structure and thermodynamics of each metal is the distribution of the remaining valence electrons between the d and p orbitals. For metals such as W, Mo, Cr, Ta, Nb, and V, the bonding energy calculations indicate[2] that the electronic configurations in the metal are close to $d^{n-1}s$ with only small contribution from p electrons. These metals form only the body-centered cubic (bcc) structure at all temperatures and pressures in confirmation of the Engel correlation and the Hume-Rothery rules,[2-5] that associate the bcc structure with electronic configurations with one s electron per atom and p electron contributions below 0.5 p electrons per atom.

The reason for the stabilization of the $d^{n-1}s$ configuration and the bcc crystal structure, where n is the number of valence electrons, can be seen in Fig. 3 which presents the spectroscopic data for the gaseous atoms of the second transition series as an example. The energies of each configuration are presented as bands because there are, in general, several spectroscopic states for each electronic configuration, corresponding to different combinations of the spin and orbital momenta of the electrons. The range of energies of spectroscopic states of highest spin multiplicity (spin momenta combined with minimum pairing) corresponding to each of the electronic configurations is shown in Fig. 3. 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 strontium, yttrium, and zirconium the $d^{n-1}s$ and $d^{n-2}ps$ configurations are close enough in energy that both configurations would be expected to be important; by the Engel correlation both bcc and hcp structures corresponding to configurations $d^{n-1}s$ and $d^{n-2}ps$, would be expected. For niobium and molybdenum the $d^{n-1}s$ configuration has become so much lower in energy than the $d^{n-2}ps$ configuration that one would expect the hcp structure to be unstable. Both configurations have the same number of bonding electrons; thus the large difference in promotion energy cannot be compensated by additional bonding energy as in the example of magnesium, where the excited ps configuration with two bonding electrons predominates over the s configuration with no bonding electrons.

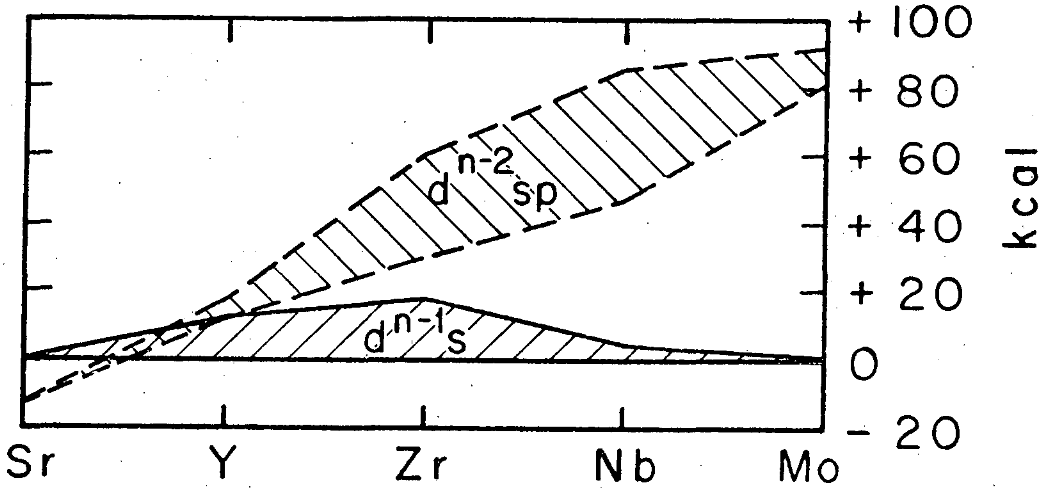

Figure 3. Relative energies of $d^{n-1}s$ and $d^{n-2}ps$ configurations for gaseous atoms of second transition series.

Likewise, it is possible to confirm the Engel correlation[3,4] of electronic configuration $d^{n-2}ps$ with the occurrence of the hexagonal close-packed (hcp) structure. Until recently, spectroscopic data for the $d^{n-3}p^2s$ configuration were known only for Y. Data are now becoming available for other elements,[7] but are insufficient to check the Engel correlation of this configuration with the face-centered cubic close-packed (ccp) structure. However, there are ample confirmations[4] of predictions of alloy behavior based on the Engel correlation for the ccp structure to clearly establish that the occurrence of bcc, hcp, or ccp structures depends upon the distribution of electrons between the d and p orbitals.

RELATION OF PHASE BEHAVIOR TO ELECTRONIC STRUCTURE

The determination of the correct electronic configuration not only allows the prediction of the crystal structures of transition metals and their alloys, but also the general thermodynamic properties that fix the stability ranges. For increasing p electron concentration, the possible thermodynamically stable crystal structure for transition metal alloys will be found in the sequence:[4] body-centered cubic (bcc) at lowest p concentration, then A15(Cr_3Si), σ(β-U) and related φ, δ, P, R, and $D8_5$ structures, χ(α-Mn), β(β-Mn), hexagonal close-packed (hcp) to cubic close-packed (ccp) at highest p concentrations. Suitable size criteria must also be met in addition to the proper range of p electron concentrations. This relationship between the proportion of p electrons among the s, p electrons and the crystal structure has been extensively reviewed.[2-7]

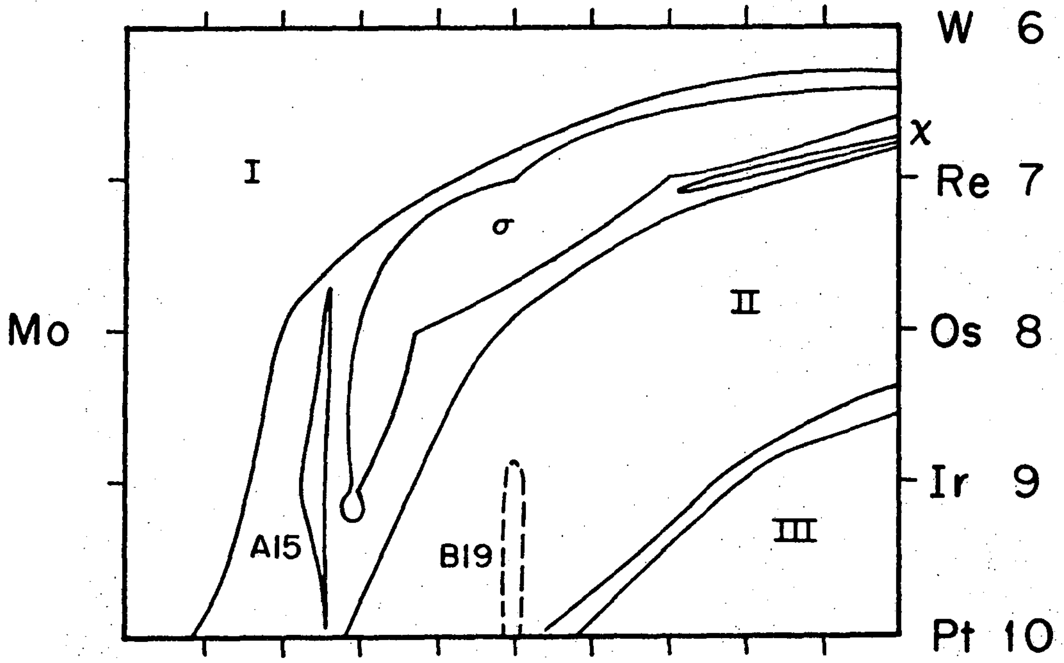

Figure 4. Multicomponent phase diagrams of molybdenum with third-transition-series metals projected along the temperature axis. Abscissa gives atomic percent of molybdenum in alloys.

The relation of the occurrence of the above phases to electron per atom concentration is illustrated in Fig. 4. The complete diagram, including temperature variation, would require a six-dimensional plot; Fig. 4 represents a projection to a two-dimensional diagram.[4] Each point corresponds to an alloy composition, with the abscissa giving the atomic percent of molydbenum and with the right ordinate corresponding to the average electron-per-atom contribution of the metals on the right-hand side, which varies from six for tungsten to ten for platinum. For example, a horizontal line at the osmium position (eight electrons per atom) represents a projection of the binary molybdenum-osmium system along the temperature axis so that the composition range of each phase region represents the maximum extent at the optimum temperature. Thus the bcc phase region extends from pure molybdenum to 20 atomic percent osmium; the A15 or Cr_3Si structure has a narrow composition range around Mo_3Os; the σ phase extends from 30 to 37 atomic percent osmium; the area labeled II corresponds to the hcp phase region from 48 to 100 atomic percent osmium. The areas between the indicated phase regions correspond to two-phase mixtures. A dotted area labeled B19 is an ordered phase region of AuCd structure which separates from the hcp phase at low temperature. A horizontal line drawn halfway between rhenium and osmium would intersect the sequence of phase regions resulting from adding molybdenum to an equimolal mixture of rhenium and osmium. The 5d transition series metals on the right side have been chosen from the adjoining elements of the same transition series to minimize the effect[2,4] of variation of atomic size and of internal pressure and thus to isolate the effect of electron concentration. If tungsten, rhenium, osmium, iridium, and platinum are mixed in varying proportions to yield an average concentration of valence electrons of 7.5 electrons per atom, then the alloy behavior upon adding molybdenum to this mixture is expected to be approximately the same as indicated by the horizontal line midway between rhenium and osmium. 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 in close agreement with all the reliable data available.[8-10] As the average electron concentration is increased by adding face-centered cubic (fcc) iridium or platinum to bcc molybdenum, the same sequence I(bcc), II(hcp), and III(ccp) is obtained with increasing electron concentration as for the pure metals, e.g. Mo(bcc)-Tc(hcp)-Rh(ccp).

If lines of equal electron concentration per atom were plotted across the diagram, they would be curved lines sloping for seven electrons per atom, for example, from rhenium on the right to a 25 percent platinum, 75 percent molybdenum alloy on the left. The electron phases such as structures σ, χ, I, II, and III have boundaries which tend along isoelectronic lines. 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.[5] Phase guides of the type shown in Fig. 4 not only condense a large amount of information into compact form, but also 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 2×10^9 multicomponent phase diagrams resulting from combinations of only 30 metals.

The difference in bonding behavior of f, d, and p electrons has been emphasized. The difference in behavior is not primarily due to the fact that f, d, or p orbitals are occupied but is due to the fact that the orbitals involved are for different main shells. Thus the 4f orbitals, for example, extend beyond the filled 4p shell to a significant extent only for cerium at the beginning of the lanthanides and gradually contract with increasing nuclear charge. The repulsion of closed 4p shells prevents any significant overlap of 4f orbitals with orbitals of neighboring atoms and very little contribution to bonding is made by the 4f electrons. The 5d orbitals project somewhat further beyond the filled 4p shell, but still not sufficiently to provide optimum overlap with orbitals of neighbors once the increasing nuclear charge in the transition metal series has stabilized and contracted the d orbital. Thus the 5d electrons do not generally bond as strongly as do the 6p or 6s electrons. The discrepancy is even greater for the 4d compared to the 5p and 5s electrons and the 3d electrons are much poorer in bonding ability than the 4p and 4s electrons. Only metals with weakly bonding electrons will show strong magnetism. With these general comments in mind, we can now consider in more detail the prediction of thermodynamic stability from knowledge of the predominant electronic configuration in the metal. There are three properties of d electrons in transition metal alloys that are important in fixing thermodynamic stability:[2-7] (1) d orbital overlap is predominantly with d orbitals of the nearest neighbors; (2) d orbital overlap and bonding is poor, but increases from 3d to 4d to 5d and can be improved by compressing the lattice to decrease the internuclear distance; and (3) d bonding capacity is lost as the number of d electrons per atom is increased from 5 to 10 since the Pauli exclusion principle requires that additional d electrons beyond the half-filled d^5 configuration be paired internally and thus not be available for bonding. Two simple examples will be used to illustrate the role of d electron bonding in the prediction of thermodynamic behavior.

The spectroscopic data for gaseous Hf indicate that two configurations, d^3s and d^2ps, are of comparable importance in the condensed phase. In agreement with the Engel correlation, Hf occurs in both the bcc and hcp structures. The bcc structure has the highest entropy due to its lower coordination number and larger vibrational contributions to the entropy and thus is the structure stable at high temperatures.[11] At the start of each transition series, the d orbital is rather extended, but the increase of nuclear charge quickly shrinks the d orbital. For Hf, the 6s and 6p orbitals extend out far enough to overlap not only with orbitals of nearest neighbors but with more distant neighbors. The 5d orbitals barely extend beyond the filled 5p subshell and overlap poorly even with d orbitals of nearest neighbors. For metals of the fourth group and on to the right of the periodic table, the bonding due to the 5d electrons is poorer than that due to 6p electrons.[2] Decrease of internuclear distance to improve the overlap of d orbitals markedly increases the bonding ability of the 5d electrons compared to 6p electrons. The compression due to application of pressure will thus stabilize the structure with the most bonding d electrons; the d^3s bcc structure of Hf will be stabilized with respect to the d^2ps hcp structure by application of pressure. The total number of d electrons per atom decreases in the order bcc > hcp > ccp. Up to the d^5s configuration of the sixth group metals, all of the d electrons are available for bonding; the effect of pressure upon stability is bcc > hcp > ccp for metals on the left hand side of the transition series for which the nuclear charge is large enough to have shrunk the d orbital sufficiently to prevent optimum overlap. Thus the metastable dp^2s ccp structures of Hf, Ta, and W would be even less stable under pressure. As there are only five d orbitals, the maximum number of unpaired d electrons available for bonding is five. Each addition of a d electron beyond five forms a pair in a filled orbital which is unavailable for bonding. For Mn, Tc, and Re, the d^5ps hcp structure with five bonding d electrons is predicted to be stabilized by pressure with respect to either the d^6s bcc or d^4p^2s ccp structure which have only four bonding d electrons. For the other metals of the right hand half of the transition series, the bcc structure has the most d electrons but the fewest bonding d electrons. For these metals, the effect of pressure upon stability is ccp > hcp > bcc or the reverse of the behavior predicted for the left half of the transition series. These predictions appear to be contrary to thermodynamics in that the order of densities at one atmosphere is not always as predicted, but the structures that are predicted to be stabilized by pressure are found to be more compressible and eventually become denser than the competing structure. The predictions of the effect of pressure upon thermodynamic stability that can be made so simply and directly from the Engel correlation have now been confirmed for every example for which complete data exist.[12-14] The enhancement of d electron bonding by reduction of internuclear distance also plays an important role in the stability of the A15(Cr_3Si) phases.[4,13]

The second example of the application of the knowledge of metallic electronic configurations to the prediction of thermodynamic behavior is the prediction of the effect of small additions of alloying metals upon the relative stability of two crystal structures. Again the distribution of electrons between d and p orbitals is decisive. We return to d^3s bcc Hf in equilibrium with d^2ps hcp Hf at 2013 K. All transition metals to the right of Hf have more than 2.5 bonding d electrons. A substitutional replacement of Hf by a transition metal to the right of Hf will result in a greater loss of d bonding in hcp Hf (two bonding d electrons) than in bcc Hf (three bonding d electrons). In all instances where data are available, these predictions of the effect of alloying upon the relative stabilities of the bcc and hcp structures have been confirmed.[8-10] All transition metals to the right of the 4th group stabilize the bcc structure of Ti, Zr, of Hf relative to the hcp structure whether the pure alloying metal has bcc, hcp, or ccp structure.

The same principles predict that non-transition metals, with no bonding d electrons, in substitutional sites will stabilize the hcp phases of Ti, Zr, and Hf relative to the bcc phase since the phase with the most d bonds per atom will suffer the most upon introduction of atoms with no bonding d orbitals. On the other hand, small atoms such as C, N, or O, that can go into interstitial sites will not interfere with d bonding; their principal effect will be their contribution of s and p electrons that will stabilize the close-packed structure over the bcc structure. Examination of the available data[8-10] confirms these predictions. Similar predictions can be made for the effect of alloying upon the phase transformation of Mn, Fe, and Co with equally good confirmation. The same principles have been shown to apply equally well for the lanthanides and actinides.[6,7]

A striking example of the ability of the valence-bond model to make thermodynamic predictions that could not be provided by other models is the prediction of extremely stable intermetallic compounds in the 4d and 5d transition series when metals of the left half of the transition series that have empty d orbitals are alloyed with metals of the right half of the transition series that have internally paired d electrons not available for bonding in the pure metal. An example would be d^4s bcc Nb with one empty d orbital alloyed with d^6ps hcp Ru with one pair of d electrons not used in bonding. In pure Ru, the filled d orbital is non-bonding because it cannot overlap with d orbitals of neighboring Ru atoms. An alloy of Zr and Ru provides the possibility of a generalized Lewis-acid-base reaction as illustrated by the classic example of BF_3 with an empty p orbital reacting with the non-bonding pair of electrons of NH_3 or the reaction of Ga with As. Metals such as Hf and Ta lack sufficient electrons to use all of their low energy orbitals in bonding and thus do not bond as strongly as W. Likewise metals such as Os and Pt have too many d electrons resulting in internal pairing of the electrons in filled orbitals which prevents their use in bonding. The use of the empty orbitals of Hf and Ta by the non-bonding electrons of Os and Pt could optimize the use of available orbitals and electrons and approach the high bonding achieved by W. The recent determination[15] of the enthalpy of formation of $HfPt_3$ to be $-135{,}000$ cal mol^{-1} is a confirmation of this prediction. Another example of unusually strong interactions is the activity coefficient of Zr in Pt alloys of 10^{-12} even at temperatures as high as 1800 K; thus the interaction reduces the vapor pressure of Zr by a factor of 10^{12} compared to an ideal solution.

LIMITATIONS OF THE VALENCE-BOND MODEL

In the short time available, I cannot discuss all of the fruitful applications of the model discussed above, and I would like to use some of the remaining time to point out some of the limitations. In the earlier discussion of the relative stabilities of different electronic configurations of tungsten and hafnium metals, the contributions of the 5d, 6s, and 6p electrons to fixing the structure and bonding enthalpy were evaluated separately, but the contributions of the d electrons, for example, were averaged with no provision for evaluating the range of contributions due to the various d electrons. Thus such a model is not of use in predicting the X-ray energy required to eject one d electron or to predict properties that depend upon the variation of density of levels with energy or momentum. However, it can be used to predict the character of the sharp X-ray spectra due to excitation of an electron from the filled 4d level of the lanthanides to a partially filled 4f level. Sugar[16] has shown that the number of lines and their distribution is very characteristic of the number of electrons in the 4f orbital. The valence-bond model provides a clear prediction[6,7] of the number of f electrons in the predominant electronic configuration for the lanthanides as well as the actinides. On the other hand, the model is not designed to predict properties that depend upon the density of levels at the Fermi surface. The emphasis is upon the average contributions of all of the types of valence electrons and not upon the few electrons at the fringe of the Fermi surface. For example, the model would not be useful for prediction of electrical conductivity or the weak paramagnetism of most metals. However, it can be adapted to provide information about strongly magnetic materials.

APPLICATION TO MAGNETIC PROBLEMS

In view of the title of this conference, it would be worth at least a few words on the use of the valence-bond model for magnetic problems. As briefly mentioned earlier, the degree of participation in bonding determines the contribution of an electron to magnetism. If, as in the example of 4f electrons, the electrons are so isolated in an inner shell of the atom that very little bonding can result from overlap of orbitals of adjoining atoms, then the degeneracy of the f level is very little changed from that of gaseous atoms with corresponding number of f electrons and the maximum spin multiplicity predicted by Hund's Rule is expected. On the other hand, for Re or Hf, for example, the 5d orbitals as well as the 6s and 6p orbitals extend sufficiently outside the closed 5p shell to provide good overlap and bonding with neighboring atoms. This strong interaction destroys the degeneracy of the free atoms and the corresponding magnetism. The 5f and 3d orbitals are intermediate in their behavior. At the beginning of the 5f or 3d periods, the orbitals are rather extended thus allowing significant bonding and destruction of the magnetism of the gaseous atoms. As the nuclear charge is increased, the orbitals are contracted to the point that overlap of orbitals and resulting bonding is greatly reduced. Whether or not significant magnetism is to be expected depends upon whether the bonding interaction is sufficiently strong to spread out the degenerate levels to energy spacings large compared to kT. With such circumstances, the Boltzmann factors for population of the levels will require full population and therefore pairing of the electrons. If the interaction is small enough to only partially remove the degeneracy and to leave a high density of levels, then significant magnetism can be expected.

Thus for the early members of the 3d and 5f series, magnetism is not expected, but magnetism is expected when increasing nuclear charge has contracted the orbitals. It has been pointed out above that increasing the pressure enhances the bonding due to d electrons by improving the overlap of the orbitals. On the basis of the improved bonding under pressure, one would predict that magnetism would be reduced. At sufficiently high pressures, one would expect all of the magnetic 3d metals to lose their magnetism. For the first half of the 5f metals that do have significant bonding due to the 5f electrons,[6,7] and residual magnetism would be expected to be reduced by application of pressure. Even for the 4f metals, a similar effect can be expected especially at the beginning of the series. The dense form of cerium that is obtained at low temperatures or high pressures is a good example. The ordinary forms of cerium metal have electronic configurations with only one f electron.[6,7] The transformation to the dense form of cerium might be ascribed to a promotion of the f electron to a d orbital. However, the estimates[6,7] of energies of electronic configurations such as dp^2s or d^2ps indicate that the promotion energies are too high to be offset by the additional bonding due to a 5d electron compared to a 4f electron. The reduction of internuclear distance upon lowering the temperature or increasing the pressure of cerium, must improve the overlap of the f orbitals sufficiently to considerably enhance the bonding contribution due to the f electrons. Thus the valence-bond model assigns the same electronic configuration to both ccp forms of cerium, but the dense form is not magnetic because of significant bonding contribution from the f electron.

The number of unpaired electrons of alloys of the lanthanides, actinides, and ferro-magnetic transition metals can be characterized from knowledge of the predominant electronic configuration and the distribution of electrons for a given configuration between paired and unpaired electrons along the lines indicated by Pauling[17] many years ago. It was noted above that non-transition metals in substitutional sites of the Hf lattice favored the configuration with the fewest bonding d electrons. The same response is found for other transition metals. However, in contrast to Hf for which the configuration with the fewest bonding d electrons is achieved by promoting d electrons to p orbitals, for metals to the right of the sixth group such as Mn, Fe, Co, and Ni, the filling of the 3d orbitals at the expense of 4p electrons is favored. This filling of the d orbitals is enhanced the greater the number of p electrons per atom of the non-transition substituent. As the strong magnetism of these metals is due to the 3d electrons, it is possible to make predictions about the variation of magnetism upon alloying. Alloys[6] of the light actinides provide an interesting possibility of appearance of magnetism upon alloying without change of electronic configuration similar to the example of cerium metal discussed above which can be magnetic or non-magnetic with the same configuration depending on the overlap of f orbitals. Thus metals such as Pa, U, and Pu do not show significant magnetism because of sufficient overlap of the 5f orbitals of adjoining atoms to provide bonding and removal of degeneracy. If they are alloyed with metals that do not have orbitals that can provide this overlap, the 5f electrons should become unpaired.

SUMMARY

A valence-bond model has been described that utilizes the spectroscopic data for the free atoms to calculate the predominant electronic configuration in the condensed phase. From knowledge of the correct electronic configurations and the bonding energies, thermodynamic data can be evaluated to predict stabilities of various structures and the effect of pressure, temperature, and alloying upon the relative stabilities of the different structures. Multicomponent equilibrium phase diagrams can be predicted and the occurrence of strongly magnetic metals can be understood.[20]

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20. This work has been sponsored by the Division of Research of the U. S. Atomic Energy Commission.

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