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A Synthesis of the Brewer–Engel and Samsonov–Pryadko–Pryadko Electron Correlations for Metals

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A synthesis of the Brewer–Engel and Samsonov–Pryadko–Pryadko electron correlations for metals is presented. Difficulties with both correlations are cleared up. In particular, abandonment of the Brewer–Engel association of $sp^2 \leftrightarrow$ fcc in favor of a correlation with the number of d electrons eliminates many of the contradictions of that correlation. In general, by placing greater emphasis on the d electrons in transition metals correlations with many solid state properties become much more straightforward.

1. Introduction

Many electron correlations of metals have surfaced in the past in an attempt to explain metallic properties such as crystal structure, cohesive energy, phase transformations and electrical behavior. Two of the most recent and, perhaps, the most successful are the Brewer–Engel correlation (*1, 2, 3, 4, 5*) and the configurational model of Samsonov, Pyradko, and Pyradko (*6*). Both are actually configurational models in that they assume the electrons in a solid, especially those in tightly bound energy states, fill the shells according to Hund's rule. There is also a greater attempt in these correlations than in many others to use physical concepts and not just match properties with numbers. However, each has weak points, some of which come close to being paradoxes in the logic of the correlation.

The Brewer–Engel correlation allows for promotion of electrons to states of larger multiplicity so that bonding between unpaired electrons will be maximized. The association[1] of $s \leftrightarrow$ bcc, $sp \leftrightarrow$ hcp, and $sp^2 \leftrightarrow$ fcc for configurations and crystal structures is made. The d states while contributing greatly to the bonding are not considered to directly affect the crystal structure. This is one of the more general points of criticism (10) since d states are more localized in a solid and have greater directional properties than the collective s and p electrons. The correlation also runs into trouble considering the crystal structures of the alkaline elements. Namely, how can the fcc configurations be justified for Ca and Sr when there are only two electrons available for bonding and the fcc structure requires three electrons (sp^2)? The Brewer–Engel correlation has also been criticized for its assignment of the configuration d^8sp^2 to

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[1] Principal Quantum numbers will not be written unless confusion might arise. Also, the superscript 1 will often be dropped in writing configurations.

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noble metals which would seem to be in disagreement with their observed diamagnetism.

To their credit, Brewer and Engel have cleared the way for the use of promoted states in metallic solids to enhance bonding. Data will be presented in a following section showing that promotion of electrons to states other than the ground state seems quite likely for transition metals.

The configurational model of Samsonov, Pryadko, and Pryadko (SPP) does not make use of promotion schemes, but maintains the ground state configuration of the atoms in the gas phase to explain crystal structures. The association of fcc to empty or filled shells, bcc to half-filled shells, and hcp to intermediate cases is made, fcc being the highest symmetry of close packed lattices would seem to go with the filled shells. However, the SPP configurational model also has problems with the alkaline metals. In this case it is necessary to invoke a d^0 state (empty state) to explain the fcc structure. The s^2 states (filled shells) could be invoked as an explanation but this would leave Mg and Be (both hcp) as contradictions. The correlation is not clear on what to do with noble metals ($d^{10}s^1$) which have filled (d^{10}) and half-filled (s^1) shells. The choice of the domination of the d^{10} makes the crystal structures of Zn and Cd ($d^{10}s^2$) contradictions!

The SPP model, however, has many good points. The choice of half-filled shells → bcc association (if we ignore the above contradictions) is actually quite good. The reason given for the preference of the bcc structure is that it is an antiferromagnetic lattice which accommodates the maximum magnetic moments of the half-filled shells (filled according to Hund's rule). This idea has support elsewhere (*7, 8*). The greater attention paid the *d* electrons allows for good correlation with most other physical properties of the transition metals.

The purpose of this paper is to provide a synthesis of the two preceding correlations. It will be shown that the Brewer–Engel and SPP correlations can be fused to yield a correlation which can be used in the same style as the Brewer–Engel correlation. However, the contradictions of both correlations will be avoided. The avoidance of the $sp^2 \rightarrow$ fcc correlation and its replacement by a more realistic correlation with *d* electrons will be seen to be a very essential point. Most of the modified correlation presented here will be done in a very qualitative manner in order to be able to present more types of correlating properties. Because the correlation can be handled like the Brewer–Engel correlation the same properties which Brewer treats quantitatively can be treated in this modification. For example, where Brewer finds ranges for hcp structures (4) ($sp^{0.7} \rightarrow sp^{1.5}$) from phase diagrams the same can be done for the *d* electron correlation presented here. However, the purpose here is not to redo all of Brewer's work, but to present a correlation which could include all his successful work as well as that of the SPP correlation and overcome the difficulties found in both correlations.

We will use simple concepts from solid state physics and valence bond chemistry throughout. We will employ as few empirical rules as possible in the process. It will in fact be interesting to see that many trends in the energy levels of atoms in the gas phase show up quite often in many different solid state properties. The result will be an electron correlation which can be related to band theory. While the SPP correlation makes some attempt to do this in general, Brewer has generally had a difficult time with band theorists (*5, 6*).

There will still remain many concepts and facts not well explained: the absence of the high-temperature bcc form for late transition metals, (which leads to) a quantitative treatment of vibrational entropy and its relation to crystal structures, treatment of electronic configurations in alloying and compounding, and, of course, ferromagnetism. Despite these shortcomings the modification presented herein is another step in the direction of relating solid state properties directly to the entities which combine to give the solid form, the atoms.

II. The Basis of the Correlation

Any good electron correlation would make use of atomic data, a simple scheme to get atomic data into solid state data and solid state experimental data to check predictions. Since solid state trends or data can also suggest correlations this aspect is presented first.

A. Solid State Data

With few exceptions all metals in the alkali, alkaline, and transition groups have bcc, hcp, or fcc crystal structures with elements of the same group often having the same structure. This immediately suggests a correlation with the filling of electron energy levels in the elements. Table I shows the crystal structures of the elements in the correlation (*9*).

The general band structure of the above metals has been studied by X-ray, photoemission and absorption, and ESCA (*11, 12, 13, 14, 15, 16, 17, 18, 19*). These show the existence of large narrow maxima in the density of states of the alkaline and transition metals which is widely accepted (20) to correspond to the d band.

The electronic configurations of the metals in the solid state have been studied to some extent by Compton scattering profile experiments. Band calculations using different electronic configurations were compared with the actual profiles for several metals (*21, 22, 23, 24, 25, 26*). The results for transition metals are that many metals in the solid appear to be not in a ground state but in a promoted state which can be represented by the configuration $d^{n+1}s^1$ (whereas most transition metal atoms in the gas phase are in a state which can be represented as d^ns^2). In particular this is stated in the references for Sc (d^2s), Ti (d^3s), V (d^4s), and Fe (d^7s). Even copper is shown

TABLE I

Element	Crystal structure	Transition temperature
K,	bcc	
Ca	fcc	448°C
	bcc	
Sc	hcp	1334°C
	bcc	
Ti	hcp	882°C
	bcc	
V	bcc	
Cr	bcc	
Mn	A12	727°C
	A13	1095°C
	fcc	1133°C
	bcc	
Fe	bcc	910°C
	fcc	1390°C
	bcc	
Co	hcp	400°C
	fcc	
Ni	fcc	
Cu	fcc	
Zn	hcp	
Rb	bcc	
Sr	fcc	215°C
	hcp	605°C
	bcc	
Y	hcp	1490°C
	bcc	
Zr	hcp	865°C
	bcc	
Nb	bcc	
Mo	bcc	
Tc	hcp	
Ru	hcp	
Rh	fcc	
Pd	fcc	
Ag	fcc	
Cd	hcp	
Cs	bcc	
Ba	bcc	
La	hcp	330°C
	fcc	864°C
	bcc	
Hf	hcp	1755°C
	bcc	
Ta	bcc	
W	bcc	
Re	hcp	
Os	hcp	
Ir	fcc	
Pt	fcc	
Au	fcc	
Hg	Rhombohedral	

(*27*) to have *d*-like bonding in the ⟨110⟩ directions.

The above data yields a starting point for the correlation of crystal structure and other solid state properties with the filling of electron energy levels in atoms. However, first some physical concepts and atomic data must be introduced.

B. Physical Concepts

The solid state data imply that there are certain methods we can use to treat electrons in metals. Firstly, the *d* band shape implies that a tight-binding view of the *d* electrons is a good approximation (*20, 28, 29, 30*) and these can be viewed as hybridizing with the *s* and *p* electrons which generate a broad flat band (*31, 32*). This will also be taken to mean that concepts such as valence bonds, localized *d* electrons and *d* orbitals all apply to *d* electrons in transition metals. Samsonov *et al.* (*6*) give both theoretical and experimental arguments for the use of these concepts and also for using Hund's rule as a guide in filling the *d* band. This, of course, makes the transition from atomic data to solid state data much more straightforward since now many atomic concepts are carried over or are strongly linked to solid state concepts for the *d* band.

The Compton scattering data combined with the previous argument for localized electrons indicates that Brewer's use of promotions to higher multiplicity states in the bonding of transition metals is correct. For this reason extensive use will be made of promotions to states in which the electrons are unpaired and more suitable for bonding.

Finally, the usual concepts of bonding due to electron orbital overlap, density of states as a function of overlap, and solid state properties as a function of density states (and therefore overlap) will be employed throughout.

C. Atomic Facts

In considering changes in electronic configurations promotion energies (*33*) must be taken into account. These yield a rough estimate of the energy states in the solid and can serve as a check on whether a configuration seems physically possible. The promotion energies can also indicate the relative positions of *s*, *d*, and *p* levels in the atomic state. In Figs. 1, 2, and 3 the energies for the promotions $d^ns^2 \rightarrow d^{n+1}s$ and $d^ns^2 \rightarrow d^nsp$ are plotted for the first, second, and third transition series respectively. These will also be referred to as *d*- and/or *p*-level energies. They will be used in the correlation to help determine the electronic configurations and to determine, qualitatively, how far the *d* orbitals extend beyond the *s* shell (34). For the purpose of bonding we always use promotions to states of maximum multiplicity and for consistency we always take the energy of the highest angular momentum state (J = maximum) for the given multiplicity. This is precisely the method of Brewer in assigning energy values to promoted states.

Using only the promotion energies in combination with the physical concepts we can now make quite a few solid state correlations.

III. The Correlation

It will be assumed that because of their highly directional properties the *d* electrons

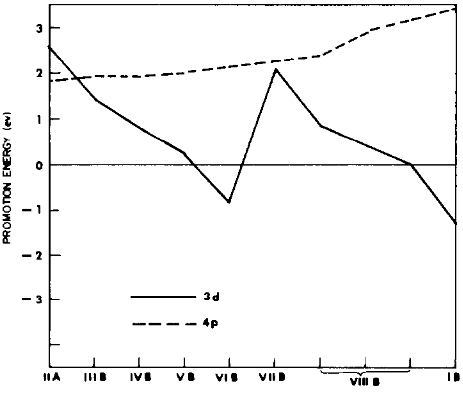

FIG. 1. Promotion energies for $3d^n4s^2 \rightarrow 3d^{n+1}4s$ (——) and $3d^n4s^2 \rightarrow 3d^n4s4p$ (– – – –).

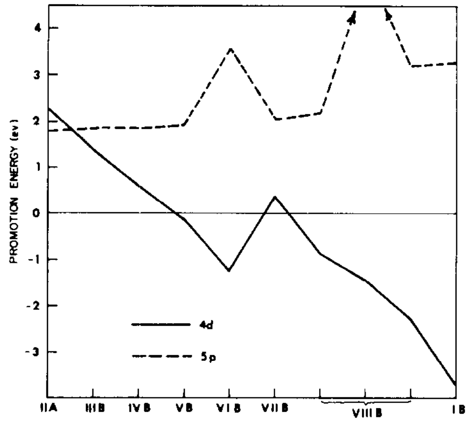

FIG. 2. Promotion energies for $4d^n5s^2 \rightarrow 4d^{n+1}5s$ (——) and $4d^n5s^2 \rightarrow 4d^n5s5p$ (– – – –).

tend to control the crystal structure for transition metals. The only case in which their control may be yielded is near a d^5 configuration. A d^5 configuration (filled according to Hund's rule) is a spherically symmetric electron distribution for the atom in the gas phase and the direction properties are lost. The Brewer–Engel correlation will be used when there is little (d^5) or no (d^0, d^{10}) d control of crystal structure. In addition, the Brewer–Engel association of $sp \leftrightarrow$ hcp will be retained since it will also be useful in showing points at which fcc$\leftrightarrow$hcp and bcc$\leftrightarrow$hcp transitions are likely to occur. The Brewer–Engel association of sp$^2\leftrightarrow$fcc will not be used for transition metals, but will be substituted by a correlation similar to the SPP fcc correlation.

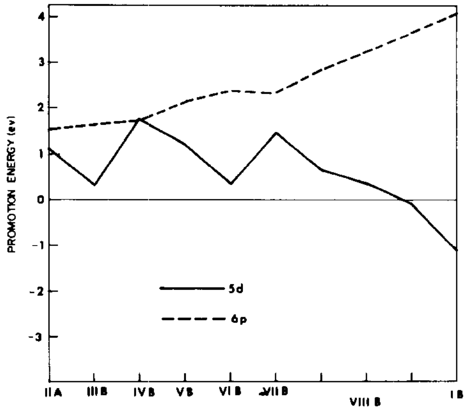

FIG. 3. Promotion energies for $5d^ns^2 \rightarrow 5d^{n+1}6s$ (——) and $5d^n6s^2 \rightarrow 5d^n6sp$ (– – – –).

The correlation for the transition metals is as follows: (1) for metals which are likely to have electron configurations in the range d^x $(0 < x < 2)$ we assign the fcc structure, (2) for metals with electron configurations at or near d^5 we assign the bcc structure, and (3) for metals of intermediate configurations of d^x $(2 < x < 4)$ we assign the hcp structure. There is much overlap in the electron concentration ranges and the determining factors in the overlap ranges will be the p electron concentration and the d-level energy since if the sp configuration is present hcp will be favored. For elements which have electronic configurations d^xs $(x > 5)$ we simply recall that the d shell is filled according to Hund's rule and the number of bonding d electrons is given by $10 - x$. Hence, for example, d^9s would be, effectively, d^{1}s and we would predict an fcc crystal structure.

In order to assign configurations to metals the Brewer–Engel concept of promotion to higher multiplicity states will be used with the aforementioned Compton profile data as a guide. Examination of the energies (Figs. 1, 2, and 3) will then determine in a qualitative manner the general electronic configurations of the metal in the solid. As in the Brewer–Engel correlation some elements will be assigned configurations with fractional numbers of electrons.

Some mention must be made of phase transformations resulting from temperature changes. Brewer (*5*) mentions that the bcc structure is the highest temperature structure for most metals since the bcc structure is more open and allows for larger atomic vibrations. It will be seen that this mechanism, while very predominant, competes at times with other possible phase changes which may occur when electrons near the Fermi surface are promoted to nonbonding states at elevated temperatures.

IV. Crystal Structures of Alkali, Alkaline, and Transition Metals

(1) Alkali Metals. These metals have the s^1 configuration with the rest of the electrons being internally paired in rare gas cores. Because these metals have no d electrons we use the Brewer–Engel correlation which demands a bcc structure.

(2) Alkaline Metals. Metals in this group are assumed to promote one s electron in order to achieve a higher multiplicity state for bonding. Be and Mg present no problem since their configurations become sp. The sp state correlates with hcp in both correlations and in Be we encounter the first case of a high-temperature bcc transformation. Calcium, Sr, and Ba present some problems for both correlations. However, Ca and Sr are easily interpreted in this modification. The energy level diagrams show that the configurations should be d^xsp^{1-x} (with x small). The modified correlation now demands an fcc structure resulting from the existence of d-type electrons. The d states must be few in number and near the Fermi surface since photo-emission and X-ray emission results (*11, 12*) do not show a large d maximum in the density of states below the Fermi level. We would expect possible transformation to hcp at elevated temperatures since the d electrons which control the fcc structure are among the first to be promoted to nonbonding states leaving mainly an sp^{1-x} configuration which correlates to an hcp structure. However, there may be competition with the bcc high-temperature structure. In the case of Sr the hcp structure predominates with the bcc structure appearing at higher temperatures. Ca transforms directly to bcc.

Ba is observed only in the bcc state. This makes it the only metal difficult to reconcile with this correlation. Unlike Ca or Sr the d^1s state is lower in energy than the d^0sp state and the fcc → (hcp, bcc) transformation would be expected to take place at a higher temperature than it does in Ca or Sr. It is possible that vibrational entropy plays a larger role for Ba and the close packed structures are found only at lower temperatures.

(3) Group IIIB and IVB Metals. Metals in Group IIIB would have a $d^{2-x}sp^x$ configuration as can be seen from Figs. 1, 2, and 3. We note from these figures that x would be small only for La because the d state here is much lower in energy than the p state. Because of the existence of a non-negligible p electron contribution the hcp structure should be well stabilized in Y and Sc. However, the lower d energy and lesser presence of p-type electrons for La would mean that the hcp state is not well stabilized. This is evident in two respects. First, the structure of La is actually double-hcp (d-hcp) in which hexagonal close packing alternates with cubic close packing. Secondly, we would expect the p states to be near the Fermi energy and electrons in these states would be among the first to be promoted to nonbonding states along with some of the d electrons. This means a configuration close to $d^{2-x}s$ is reached eventually, i.e. the stability of the d-hcp structure diminishes as temperature increases. The d-hcp → fcc transformation is thus to be expected at higher temperatures. All three metals in this group undergo the high-temperature transformation to bcc.

The metals of Group IVB have a $d^{3-x}sp^x$ configuration with x about equal for Ti and Zr and much larger for Hf since the d-level energy is much nearer the p-level energy for this metal. These values are near the intermediate d electron numbers which require hcp structures. The presence of the sp configuration stabilizes those structures. The relative stability is again evident in the temperatures of transformation to bcc structures. Hf does not transform to the high temperature bcc state until a temperature much greater than the transformation temperatures of Ti and Zr.

(4) Groups VB and VIB Metals. In Group VB we can safely assign the configuration d^4s

to V and Nb. In both the Brewer–Engel correlation and the SPP correlation this corresponds to a bcc structure. Ta, on the other hand, should be $d^{4-x}sp^x$ with x not small. Thus in this case it is not clear whether the structure should be hcp or bcc. Ta can be considered a borderline case just on the bcc side of the border. This will be seen to be consistent with the cases of Tc and Re.

The VIB metals should have the d^5s configuration since the p levels are high in energy for all three metals. This also requires a bcc structure according to both correlations and this is found in all three metals.

(5) Group VIIB Metals. Re and Tc should have a $d^{6-x}sp^x$. As explained in the remarks this is equivalent to a $d^{4+x}sp^x$ configuration. Again, these are borderline cases. However, both Re and Tc have d-level energies which are higher than their corresponding VB series mates, Ta and Nb. This means that the p electron population is larger for Re and Tc. This would stabilize the hcp structure.

Mn exhibits complex structures below 1095°C. Considerations both of larger than ideal coordination numbers in these Mn structures and magnetic moments in the solid state [36] suggest two or three different kinds of Mn atoms in the unit cell. This may be a case in which certain atoms remain permanently in a promoted or unpromoted state. The large promotion energy for $d^5s^2 \rightarrow d^6s$ or d^5sp implies considerable change in size for the Mn atom. Such size differences would be necessary to get the greater than ideal coordination numbers found in the Mn structures.

The absence of the high temperature bcc phase transformation for Re and Tc can not be explained presently. While the d^5sp and d^6s states are relatively close in Re, the energy difference in Tc is somewhat larger. It would not seem unreasonable, then, to expect a hcp → bcc transformation for Tc at elevated temperatures.

(6) Group VIIIB Metals. In this group we find the d levels sinking fast as we move across each series while the p levels rise. Hence, we expect little sp contribution to hcp stability and hcp structures would come only near the intermediate numbers of d electrons (d^{7-8}). Because of the energy level considerations the groups can be assigned the following configurations: d^7s (Fe group), d^8s (Co group), and d^9s (Ni group). We assume that Pd requires the promotion $d^{10} \rightarrow d^{9s}$ for bonding. Except for Fe, all assignments correlate well with the corresponding crystal structures. Co has the smallest d-level–p-level energy difference in its group, which is consistent with its hcp structure. However, its relatively low fcc transformation temperature is not surprising in light of the energies in Fig. 1. The particular case of Fe appears to result from ferromagnetism and has been successfully attacked elsewhere [37].

(7) Group IB Metals. Since d bonding has been shown to exist in Cu (*23*), it is not unreasonable to expect a $d^{10-x}sp^x$ configuration for Cu, Ag, and Au with x being small. This configuration is also consistent with the rules given for fcc structures.

(8) Group IIB Metals. Both Zn and Cd have a filled shell which is very low in energy and probably does not participate in bonding. Therefore a promotion of $s^2 \rightarrow s^{2-x}p^x$ is required for bonding and like Be and Mg these have the hcp structure resulting from sp configurations. For Hg the promotion energy for $s^2 \rightarrow sp$ is extremely large and the solid state configuration must be very close to s^2. In this case Hg has an almost closed shell and this is probably the only place in the periodic table other than the noble gases where the SPP correlation of fcc↔closed shell holds. The rhombohedral structure of Hg is simply an fcc cell stretched along one of its threefold axes. The same type of elongation occurs in Zn and Cd.

Table II lists all the elements discussed and their corresponding qualitative electronic configurations.

TABLE II

APPROXIMATE SOLID STATE ELECTRONIC CONFIGURATIONS OF THE ALKALI, ALKALINE AND TRANSITION METALS ARRANGED BY ELEMENTAL GROUP NUMBER. x IS A FRACTION WHOSE SIZE IS DEPENDENT ON THE d- AND p-LEVEL ENERGIES OF FIGS. 1, 2, AND 3

							VIIIB				
IA	IIA	IIIB	IVB	VB	VIB	VIIB				IB	IIB
K d^0s	Ca d^xsp^{1-x}	Sc $d^{2-x}sp^x$	Ti $d^{3-x}sp^x$	V d^4s	Cr d^5s	Mn d^6s + d^5sp	Fe d^7s	Co $d^{8-x}sp^x$	Ni d^9s	Cu $d^{10-x}sp^x$	Zn $d^{10}sp$
Rb d^0s	Sr d^xsp^{1-x}	Y $d^{2-x}sp^x$	Zr $d^{3-x}sp^x$	Nb d^4s	Mo d^5s	Tc $d^{6-x}sp^x$	Ru d^7s	Rh d^8s	Pd d^9s	Ag $d^{10-x}sp^x$	Cd $d^{10}sp$
Cs d^0s	Ba d^xsp^{1-x}	La $d^{2-x}sp^x$	Hf $d^{3-x}sp^x$	Ta $d^{4-x}sp^x$	W d^5s	Re $d^{6-x}sp^x$	Os d^7s	Ir d^8s	Pt d^9s	Au $d^{10-x}sp^x$	Hg $d^{10-x}sp^x$

V. Cohesive Energies

The cohesive energies in this modification can be shown to follow trends similar to those developed by Brewer. However, first it will be necessary to examine some statements concerning binding energy of the noble metals and the Brewer–Engel theory.

It is argued, by Brewer, that for the noble metals to obtain their cohesive energies extensive promotions to states like d^8sp^2 are necessary in the solid since these states have more electrons available for bonding. In contrast, Brewer argues, configurations like $d^{10}s$ would yield a lower cohesive energy since the only electrons available for bonding are the s electrons. The $d^{10}s$ case is then compared to the case of the alkali metals which have only one s electron and "as a result" have low cohesive energies.

There is another way to view this problem. Assume first that the noble metals remain $d^{10}s$ or nearly so in the solid state. Now examine the differences in the cohesive energies of alkali and noble metals and the dissociation energies of diatomic molecules of the same metals. It is reasonable to assume that in the transformation from a diatomic gas to a solid state crystal there should be an increase in binding energy since the atoms in the solid state have higher coordination numbers (we can ignore promotion energies since we are examining only cases of s^1 bonding). If these metals have an s^1 configuration in both the diatomic and solid state it is reasonable to expect the increase in binding energy in going from the diatomic molecule to the crystal state to be proportionally the same for each metal. This is because the bonding electrons retain the same symmetry (s^1) and the differences in energies for different crystal structures are only a few percent of the total bonding energy (38). Table III gives the bond strengths for diatomic molecules, cohesive energies for crystalline solids, and the ratio of the two for alkali, noble, and some other transition metals for which data is available. The ratios of the two energies are extremely close for the alkali and noble metals, especially for those of the same series. However, metals which promote electrons to states of different symmetries other than s^1 are seen to have very different energy ratios. Hence, since the noble metals increase their binding energies by the same factor as the alkali metals, the $d^{10}s$ configuration is consistent with the cohesive energy data. The problem thus resolves into explaining the diatomic bond for noble metals.

TABLE III

DIATOMIC BOND STRENGTHS, COHESIVE ENERGIES, AND THEIR RATIOS[a]

Element	Diatomic bond strength (kcal mole)	Cohesive energy (kcal mole)	Ratio: $\frac{\text{cohesive energy}}{\text{diatomic bond}}$
Li	24.6	38.2	1.55
Na	18.4	26.0	1.41
K	12.8	21.7	1.69
Rb	12.2	20.2	1.66
Cs	11.3	19.2	1.70
Cu	46.6	80.8	1.73
Ag	41	68.3	1.67
Au	52.4	87.6	1.67
Be	17	76.9	4.52
Mg	8 (?)	35.3	4.41
Sc	25.9	80.1	3.09
Y	38.3	97.6	2.54
La	58.6	101.9	1.73
Ti	34	112.2	3.30
V	58	122	3.59
Cr	<37	94.5	>2.55
Mn	4	66.9	16.7
Fe	24	99.4	4.14
Co	40	101.7	2.54
Ni	55.5	102.3	1.84
Pd	33 (?)	89.9	2.72
Zn	7	31.0	4.42
Cd	2.7	26.8	9.92
Hg	4.1	15.41	3.76

[a] Data for diatomic bonds is from "The CRC Handbook of Chemistry and Physics," 54th ed., 1973–1974, CRC Press, Cleveland, Ohio. Cohesive Energies are from reference 39.

Following Brewer we first examine the effective bonding of *s* and *p* electrons as a function of group number in each series. Like Brewer we consider the *s* and *p* electrons to contribute equally to the cohesive energy. We take as starting values the cohesive energies (*39*) alkali and alkaline earth metals. However, unlike Brewer we do not use the Zn group for the other end of the series. The noble metals are used instead. This is done for two reasons. The most important is that the IIB group metals have crystal structures which are severely elongated along one axis and as a result may not reflect the actual bonding conditions found in the transition series. The second reason is that the noble metals have been shown to be primarily $d^{10}s$ in configuration and, hence, the *s* bonding is easily calculated since there are no promotions. We then extrapolate on a smooth curve between the alkaline metals and the noble metals to give the *s*, *p* bonding energies for the transition series. These graphs are shown in Fig. 4 for all three transition series.

The *d* binding energies can now be calculated as a function of group number for each series by the following formula (*2, 4, 5*)

$$D = \frac{C + P - nS}{m}$$

where D = the *d*-electron contribution to the binding energy per *d* electron available for bonding, C = cohesive energy (*39*) of the element, $S = s$ and p binding energies for that element, n = total number of s and p electrons per atom in the solid, and m = number of *d* electrons available for bonding in the solid state. For simplicity we take all metals in the transition series to be in the $d^{n+1}s$ configuration. The *d* binding energies are shown for these configurations in Fig. 5.

Examination of Figs. 4 and 5 and comparison with those given by Brewer (*4*) for electron binding energies show that the basic trends in binding energy for the

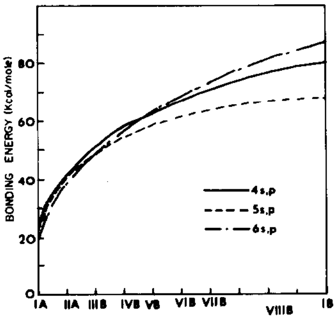

FIG. 4. s and *p* electron bonding energies for the 3*d*, 4*d*, and 5*d* transition series.

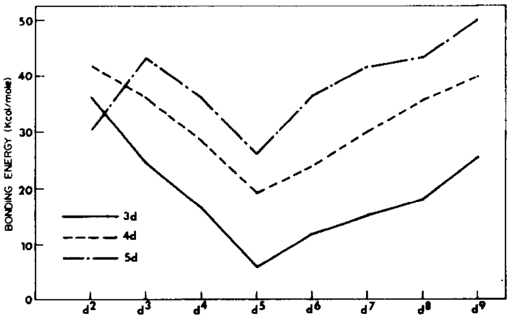

FIG. 5. *d* electron bonding energies for all three transition series.

different types of electrons are the same in both correlations. The differences are that the *s* and *p* binding energies are shifted to higher values and the *d* binding energies are shifted to lower values. However, because the basic trends are the same all conclusions in the Brewer-Engel correlation which rely solely on these trends and do not depend on the $sp^2 \leftrightarrow$ fcc correlation can now be carried over into this synthesis of correlations.

VI. Some Other Metallic Properties

A. Conductivity

It is well known that the *d*-band position can greatly affect the conductivity of transition metals. This, of course, results from the *d* band's large, narrow density of states which if present at the fermi level can impede electrical conduction. Since we are assuming that all transition metals are in a $d^{n+1}s$ state (or nearly so) we would expect the *d*-level energies in Figs. 1, 2, and 3 to be reflected in the solid by the relative position of the *d*-band peak with respect to the fermi level. The *d* band hybridizes with the relatively broad *s*–*p* band which has a low density of states so that if the *d*-level energy is low we would expect mostly *s*- and *p*-type electrons near the fermi level. If, on the contrary, the *d*-level energy is high we would expect mostly *d*-type electrons near the fermi level. Thus, we should expect conductivity to vary as an inverse function of the *d*-level energies. Indeed, as Fig. 6 shows, the conductivities correlate very well with the *d*-level energies in the manner mentioned above. We find a relative maximum in the conductivity at d^5 (VIB group) where the *d*-level energy is a relative minimum. As the *d*-level energies rise sharply for the VIIB metals so the conductivities of the metals fall sharply. Again the conductivities rise as the *d*-level energies fall off in the late transition metals. In the noble metals the relative levels of the *d*-electron energies are apparent in the relative conductivities of these metals. The *d*-level energies decrease from Au → Cu → Ag and the conductivities increase from Au → Cu → Ag. At first it may seem that the alkaline metals do not agree with the correlation, but it must be remembered that their configurations are not $d^{n+1}s$, but $d^x sp^{1-x}$ (with x small). Hence, we expect little *d* contribution at the fermi level. However, even here the relative *d*-level energies are reflected in the conductivities. The *d*-level energies decrease from Ca → Sr → Ba, meaning that x is largest in the $d^x sp^{1-x}$ configuration for Ba. Correspondingly, the conductivities decrease from Ca → Sr → Ba.

On this basis we would be correct in concluding that the *d*-level energies do reflect the *d*-band position in the solid and

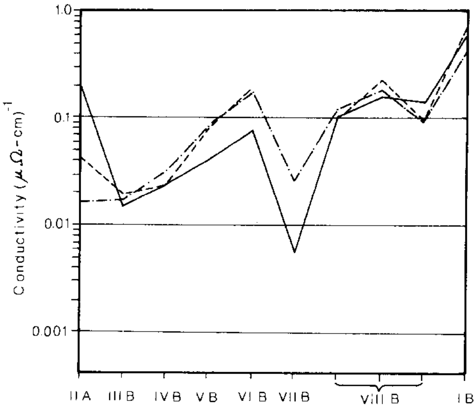

FIG. 6. Conductivities of the 3*d*, 4*d*, and 5*d* transition metals as a function of group number.

hence also the relative size of the density of states at the fermi level. Figure 7 is a qualitative diagram of the density of states for a transition series as a function of the group number based on Figs. 1, 2, and 3.

B. Superconductivity

We can now give an example of an area which was originally treated by the Brewer–Engel theory and which can now be taken over into this modification and clearly interpreted. The relation of superconductivity to *d* bonding has already been considered (*40, 41*). In particular, Gualtieri (*40*) has shown that the net attractive potential, *V*, for electrons in Cooper pairs can be correlated to bonding of *d* electrons in transition metals using the Brewer–Engel theory. Because the correlation was done for groups IIA → VIIB and is especially good in the intermediate groups where there are no fcc structures the same correlation can be made with the modifications presented here.

The critical temperature for superconductivity is given by (*42*)

$$T_c = (\theta_D/1.45)\exp(-1/N_0V)$$

where T_c = critical transition temperature for the onset of superconductivity, θ_D = Debye temperature, N_0 = density of states at the fermi level, and V is the net attractive potential mentioned above. Figure 8 shows that T_c varies by orders of magnitude across the transition series. θ_D does not vary this much and the largest changes in T_c must result from the exponential term $(-1/N_0V)$ (*40*). A few calculations with typical values for T_c and θ_D show that even small changes in N_0V will yield large changes in T_c. If we now take Gualtieri's supposition that V and *d* electron bonding are directly related for transition elements we can easily explain the trend in T_c for the transition series. As a first approximation N_0V should be a constant (*40*). Since the density of states varies inversely as *d* overlap and V is proportional to *d* overlap their product should not vary as a function of *d* bonding. However, this simple argument neglects the fact that the *d* band is hybridizing with a broad flat *s,p* band and it is the relative position of the *d* level which will help determine N_0 as shown in the previous section on conductivity. Hence, we would expect the qualitative variation of N_0V to be the same as the variation of N_0 shown in Fig. 7. The exponential of $-1/N_0V$ should appear as shown in Fig. 9. This will, of course, be modulated by θ_D, but, as mentioned before, θ_D does not vary radically across a transition series. We see then that the controlling factor in transition metal

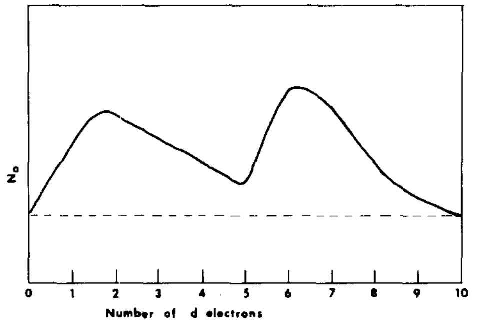

FIG. 7. Qualitative variation of N_0 (the density of states at the Fermi level) with number of *d* electrons.

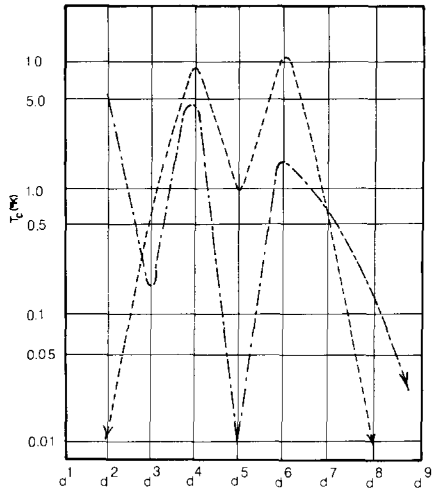

FIG. 8. Critical superconducting temperatures (T_c) for the 4*d* (– – – –) and 5d (— — —) transition metals (42, 38).

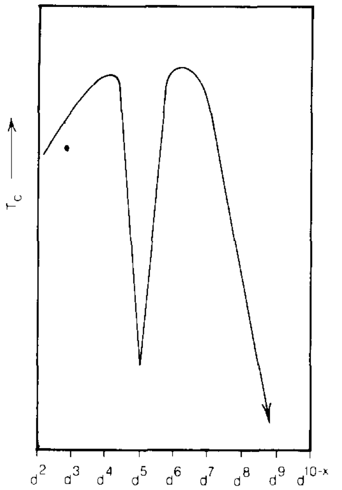

FIG. 9. Qualitative variation of $\exp(-1/N_0V)$ as a function of the number of d electrons.

superconductivity is the d-level energies. In addition, we can also see why the better conducting metals at the end of the transition series have very low T_c's. The d band sinks far below E_F leaving basically s states at E_F to generate low N_0 values. Generally T_c values do not fall off as fast in the $5d$ series as in the $4d$ series as we move past mid-series toward the noble metals. This is again reflected in the differences in d-level energies for these series (see the trends in Figs. 2 and 3).

We must note that the above explanation for the minimum in T_c at the d^5 configuration is clearer than that of Matthias (*42*) or Gualtieri (*40*). Their reasoning is that the stability of the d^5 configuration "interferes" with superconductivity by decreasing N_0. However, here using d-level energies we can see why N_0 decreases. The stability of the d^5 configuration is reflected in its relative lower energy in the atom. The d^5 case which was previously presented as a special case is now seen to be the result of more general trends in the d-levels.

C. High-Pressure Phase Stability

In an article on phase stability of rare earth elements at high pressures Hill (*43*) showed that the Brewer–Engel theory is faulty in its high-pressure phase stability predictions. The basic argument by Brewer is that at higher pressures the d–d overlap is increased and configurations which increase the number of d electrons in the solid are to be preferred. This generally means a trend toward bcc at high pressures, since to increase the d population p states are sacrificed leading to configurations which approach $d^{n+1}s$ in the solid. The prediction works well with Ti, Zr, and Hf, but consideration of the rare earth metals leads to trouble since these tend to change to fcc or at least to structures which are closer to cubic close packing. Figure 10, taken from Hill (*43*, shows the general trend for phase transformations at high pressures across the rare earth series. These contradict the Brewer–Engel correlation of bcc$\leftrightarrow s^1$. Again it is the unwieldy $d^{n-1}sp^2 \leftrightarrow fcc$ correlation which causes the trouble.

The modification presented here can also be used to predict high-pressure phase changes. Like Brewer we need only argue that under pressure transitions of electrons

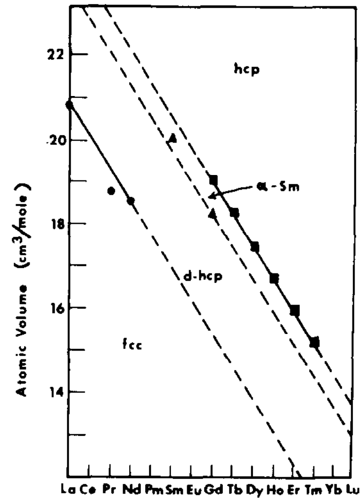

FIG. 10. Generalized phase diagram for the rare earth metals as given by Hill (*43*). Squares show transformations hcp → α-Sm; triangles, α-Sm → d-hcp; and circles, d-hcp → fcc.

$p \rightarrow d$ (or f states, if available) take place both because of increased d bonding and because these states are generally lower in the energy and hence transitions to them produce a smaller atom. In this way we agree with Brewer that Zr, Ti, and Hf should have a more stable bcc phase at higher pressures. However, in the rare earth series where the transitions would produce configurations tending towards d^2s, f^1d^1s and f^2s we would expect the hcp structure to become unstable and structures closer to fcc (which correlates to a small number of d electrons) to become more prevalent. McWhan and Stevens (*44*) state that the sequence of structures hcp → Sm → *d*hcp → fcc can be viewed as a progression from hexagonal to cubic close packing. This sequence is the sequence of phase changes in the rare earths upon increasing pressure. This is in full agreement with the modification presented here. Further study on the *d*- and *f*-level energies of the rare earths should shed light on individual rare earth structure preferences at high pressures.

D. Alloying and Compounding of Metals

A general treatment of alloying and compounding would be too vast a topic to be fully treated here. We do note that the methods of Brewer (phase stability as a function of electron concentration, internal pressures, solubilities, etc.) can be transferred to this modification. We will, however, treat two specific cases: binary alloying between noble metals and group IIB metals and intermetallic compounding. The former shows that this modification can be used with methods like those in the Brewer–Engel theory. The latter shows that there can be differences in interpretation between the Brewer–Engel theory and this modification.

The β-brass structures between noble metals and Zn and Cd are explicable by considering the fact that the promotion $s^2 \rightarrow sp$ in Zn and Cd is very high in energy compared to the few holes in the d band of Cu ($d^{10-x}sp^x$). Upon addition of Zn to Cu we would then expect some electron transfer Zn → Cu filling the d band. We would reach a Zn concentration at which the d electron influence on the structure would be vastly diminished due to internal spin pairing of the d electrons in Cu. At this point the electronic configuration would be primarily sp^x with x small and we would expect bcc-like structures (CsCl, for example) to appear which they do in most IB–IIB binaries.

Examination of the *d*-level energies across the transition series in light of the above-mentioned electron transfer leads one to suspect highly stable compounds would form between constituents of opposite sides of the transition series. This is known to be true, especially for the 4*d* and 5*d* series (*4*). This "ionic" type of transfer would take place on the d level and may even be enhanced by appropriate stoichiometry. An extreme example of this are the Hf/Zr–Pt/Pd intermetallics (*46*) such as $HfPt_3$ or $ZrPd_3$. Not only is the *d*-level energy vastly different for any two constituents, but the d^3 and d^9 configurations help stabilize the stoichiometry. Since the electron transfer is (Hf, Zr) → (Pt, Pd) the low energy d^9 level of (Pt, Pd) can be taken to be a hole which acts as a sink for one of the (Hf, Zr) electrons. Hence, the d^3 configurations of (Hf, Zr) demand three (Pt,.Pd) atoms.

This analysis of transition metal compounding is diametrically opposed to Brewer's interpretation. He suggests that electron transfer is from the late transition metals to the early transition metals, the reverse of the above argument. In this way, Brewer argues, the compounds approach a d^5 (average) configuration which is considered the reason for their great stability. It should be noted that the arithmetic of the situation enables either this modification or the Brewer–Engel correlation to predict roughly the same stable compounds. This modification requires that for an $A+B$ reaction with $A =$ an early transition metal and B = a late transition metal we should have $n_d(A) = n_h(B)$ for the greatest stability (where $n_d(A)$ = the number of bonding d electrons for A and $n_h(B)$ = the number of holes in the d shell of B). Since $n_h(B) = 10 - n_d(B)$, where $n_d(B)$ = total number of d electrons for B, we generate Brewer's requirement that $(n_d(A) + n_d(B)]/2 = 5$. There will, of course, be some differences since n_d is not the same in both correlations, but the values are close enough that either one will predict roughly the same compounds.

The question is which interpretation of the physical events is correct? The ionic transfer of this modification finds support from two sources. First, the electronegativity differences in the early and late transition metals suggest electron transfer of the type required by this modification. Secondly, an empirical approach to the calculation of heats of formation in solid alloys of A. R. Miedema *et al.* (*45*) which correctly predicts the heats of formation of the (Hf, Zr)–(Pt, Pd) compounds suggests that the good stability of these intermetallics results from the ionic type of transfer of electrons mentioned above. As far as it is known there is no outside support for the reverse transfer implied by Brewer.

V. Conclusions

We have shown that by using the SPP correlation for the transition metals we can modify the Brewer–Engel correlation in such a way as to yield a correlation which can be used in the same style as the Brewer–Engel correlation. The advantage is that we now have a correlation which can accomplish everything the two previous correlations could for the transition metals, but which carries none of their contradictions or difficult concepts (the reverse transfer of electrons for compounding and the invoking of empty states, d^0, for example). In particular the abandonment of the $sp^2 \leftrightarrow$fcc correlation and its replacement with a more realistic correlation with the d electrons immediately eliminates many problems.

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