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A MOST STRIKING CONFIRMATION OF THE ENGEL METALLIC CORRELATION

Leo Brewer

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A Most Striking Confirmation of the Engel Metallic Correlation

Leo Brewer[†]

Abstract

The Engel correlation between electronic configurations and structures of metals and alloy crystal structures is examined critically. Exceptions and inconsistencies listed by Hume-Rothery are shown to be due to improper application of the theory. For a group of 40 adjoining metals, more than 90% of the predictions of the theory are found to be accurate. A striking confirmation of the theory is the demonstration of intermetallic compounds with enthalpies of formation from -50 kcal per mole up to perhaps -100 kcal per mole.

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I wish to thank Professor W. Hume-Rothery[1] for calling attention to my recent papers on metallic bonding and intermetallic compound formation.[2,3,4] Although Professor Hume-Rothery ends his note with a discouraging tone, his review, in fact, constitutes, after correction of several errors, a strong support for the Engel correlation of the electronic configurations and crystal structures of the metals as the careful reader can verify for himself. It is unfortunate that Professor Hume-Rothery based his note on the manuscript which I sent to him before publication and that he did not refer to the published paper.[3] Most of the points raised by him also came up in the discussion with Professor J. Friedel following the presentation of the paper at the June 1964 High-Strength Materials Conference. As the published paper includes the discussion which deals with these questions in considerable detail, there is no need to repeat the discussion here.

It would, however, be worthwhile to correct some of the errors and misapplications of the Engel correlation in Hume-Rothery's paper and to present a very striking confirmation of the Engel correlation. The application of the Engel correlation can be illustrated by Figure 1 where the dotted region labeled $d^{n-2}sp$ represents the range of energies of excited atomic states corresponding to the electronic configuration $d^{n-2}sp$ where n is the total number of valence electrons. The area labeled $d^{n-1}s$ represents the range of levels corresponding to the configuration $d^{n-1}s$. In both instances, only states of highest multiplicity are considered as being important for metallic bonding. For Zr, as an example, the range of energies in the dotted region corresponds to the six levels ^5D, ^5P, ^5S, ^5G, ^5F, and ^5D of the d^2sp configuration while the bold lines correspond to the two states ^5F and ^5P of the d^3s configuration. For Sr, Y, and Zr where the energy ranges of the $d^{n-2}sp$ and $d^{n-1}s$ configurations lie closely together, the energies of the bcc and hcp structures must be close. One would predict both structures in agreement with observation. For Nb and Mo, the d^3sp and d^4sp energies are so high compared to the d^4s and d^5s energies, respectively, that one would predict the hcp structures to be very unstable, again in agreement with observation. A complete review of promotion energies of the $d^{n-1}s$, $d^{n-2}sp$, and $d^{n-3}sp^2$ electronic configurations for the transition metals and a discussion of the minor differences of bonding strength of s, p, and d electrons will be presented in a paper shortly.[5]

Hume-Rothery's statement (Page 1039) that the Engel correlation is assumed to be valid only at high temperatures demonstrates that he has not understood that the Engel correlation makes thermodynamic predictions and therefore must be valid for the entire temperature range. When the correlation predicts that the energies of the hcp and bcc structures of Sr, Y, and Zr are close, both structures are to be expected, but entropy considerations fix the bcc structure as the high temperature form when there are no magnetic contributions since the structure of lower coordination will have a larger vibrational contribution to the entropy. In reference 3, the high temperature applications of the Engel correlation have been emphasized for the practical reason that predictions of multicomponent phase compositions can be compared with experiment only at temperatures high enough to allow reliable equilibrium values to be attained experimentally. In addition, low temperatures were deemphasized to avoid a much lengthier paper that would be required for a more detailed discussion of the many low temperature phases with very special ordering of the different components.

This basic misunderstanding of the thermodynamic aspects of the Engel correlation accounts for most of the misstatements in Hume-Rothery's paper. For example, the misstatement (Page 1042) that the Engel correlation would predict the cohesion to be stronger in Ag than in Cu is based on an incomplete thermodynamic cycle. The net cohesion is the result of the difference between the promotion energy required to produce the atom in its bonding valence state and the resulting bonding energy when the atoms are bonded. Hume-Rothery has neglected the promotion energies. The spectroscopic data[5,6] show that the promotion of an electron from a d orbital to an s orbital requires 50 to 60 kcals per gram atom less energy for Cu and Au than for Ag. Likewise the promotion of a d electron to the p orbital can be achieved with 40 to 50 kcals less energy for Cu and Au than for Ag. As discussed on Page 21 of reference 3, the fact that the abnormally low enthalpies of atomization of Pd and Ag, compared to elements above or below in the periodic table, can be attributed to the abnormally high promotion energies of the d electrons is a very strong confirmation of the validity of the valence-bond approach and the utility of the promoted valence state.

Hume-Rothery's discussion (Page 1040) of Mn is likewise in error due to the fact that he has neglected to check the spectroscopic data to find out the actual magnitude of promotion energies. His statement that a configuration which involves an opening of the d^5 half-filled shell would be very improbable is contradicted by the fact that the

d^4s^2p configuration of Re is only 38 kcal above the d^5sp configuration. Reasonable assignments of bonding energies due to the additional bonding p and d electrons will easily account for the observation that the net atomization enthalpies of bcc and fcc Mn are very close. The remainder of Hume-Rothery's following discussion can be excluded on the same basis. It is clear that he has not actually looked up any of the pertinent spectroscopic data. In addition, it is surprising that he would make the statement (Pg. 1040) that hcp Fe is non-existent. The stabilization of hcp Fe at moderate pressures is well established[7] in confirmation of the prediction from the Engel correlation that the atomization enthalpy of the hcp structure would be only a relatively small amount higher than that of the bcc structure.

The question of whether copper, silver, and gold could be one-electron metals has been discussed adequately in references 2 and 3 and particularly in the discussion with Professor Friedel which is given in reference 3. At this point it should be sufficient to merely offer Table I in evidence on this question. The melting points and distances of nearest approach are those listed by Hansen and Anderko.[8] The atomization enthalpies are from reference 3. The increase in melting point and atomization enthalpy and the decrease in distance of nearest approach in every instance in going from Group IIB to IB completely eliminates any possibility of only one electron per atom being used for bonding in the examples of Cu, Ag, and Au. Many other properties could be cited in confirmation. The comparison of groups IIA and IA show the reverse changes as would be expected. As is pointed out on Pg. 73 of reference 3, the so-called one electron model of copper refers only to the upper

Table I

Comparison of Melting Points, Heats of Atomization, and Distances of Closest Approach for Solid Metals of Groups IIB and IB, and Groups IIA and IA.

Zn	Cu		Ca	K	
420°	1083°	°C	850°	64°	°C
31	81	kcal/mole	42	21	kcal/mole
2.66	2.56	Å	3.94	4.63	Å
Cd	Ag		Sr	Rb	
321°	961°	°C	770°	39°	°C
27	68	kcal/mole	39	19	kcal/mole
2.98	2.89	Å	4.31	5.00	Å
Hg	Au		Ba	Cs	
-39°	1063°	°C	710°	30°	°C
15	87	kcal/mole	42	19	kcal/mole
3.01	2.88	Å	4.35	5.25	Å

fringe of the Fermi surface and ignores the strong binding due to the remainder of the valence electrons. The electrons that are bonding the atoms together may be largely in filled bands just as the bonding electrons of the N_2 or NO molecules are in filled molecular orbitals, but they play the major role in determining the structure and other properties of the metal even though they may play a minor part in some electrical properties. Any contention that Cu, Ag, and Au are bonded by one electron per atom clearly ignores the bulk properties of these metals.

If we include the alkali and alkaline earth metals discussed by Hume-Rothery plus the thirty transition metals discussed in reference 3 extended through Cu, Ag, Au, Zn, and Cd, we are considering a total of 40 metals. A total of 120 predictions are involved in regard to the stabilities of the bcc, hcp, and fcc structures. Hume-Rothery has listed six instances in Groups IA and IIA where the predictions of the Engel correlation are apparently contradicted. I have reservations about the experimental evidence of some of the reported contradictions, but I am satisfied to have the correlation judged on his count. In view of the fact that no other theory has accounted for even a quarter of the structures, a theory with an accuracy of well over 90% should certainly have some promise. It is indeed remarkable that such a high success should be achieved on the basis of simply considering the electronic configurations in the gaseous atom that would be available for bonding. It would be expected that additional factors, particularly in weakly bonded metals, would play some role in affecting the resulting structure. Hume-Rothery and his colleagues[9] in a paper which provides the best theoretical confirmation of the Engel correlation to date encountered the same difficulties. At this time, it will suffice to merely quote their explanation (Pg. 156 of ref. 9) of the six contradictions: "At the beginning of each period we must expect the factors that determine the crystal structure of the rare gases......to be relatively more important ......We may expect an irregular correlation for the groups IA and IIA." Since there is no ready explanation for the structures of the rare gases, such a statement leaves ample room for the few apparent exceptions.

Additional corrections to Hume-Rothery's paper could be listed. As any reader who has carefully studied reference 3 can readily make these corrections himself, additional comments will be limited to those that relate to a striking new experimental confirmation of the Engel correlation. The application of the Engel correlation to transition metal alloy systems[3] yields the prediction that intermetallic compounds of metals of the second and third transition series, produced by combining transition metals from the left of the periodic table with transition metals from the right of the periodic table, will be unusually stable. The transitions metals of the fourth and fifth periods and groups 1-7, Rb to Tc and Cs to Re, use all of their valence electrons in bonding while the transitions metals Ru to Ag, Os to Au do not use all of their valence electrons for bonding in the pure metals since some of the d electrons are paired internally and are not available for bonding. The differences between the transition metals from the left and right sides of the periodic tables can be best summarized in terms of incomplete use of available bonding orbitals and full use of available electrons on the left side and incomplete use of electrons and full use of bonding orbitals on the right side. A mixture of the two types of metals will allow an electron transfer from the metal with a surplus of electrons to the metal with low-lying vacant orbitals to make fullest use of all electrons and all orbitals. As an example, we may consider a mixture of Zr and Ir. According to the Engel correlation, the electron configuration of Zr in the hcp structure is d^2sp. The configuration for Ir in the fcc structure is d^6sp^2 with only seven electrons available for bonding since a pair of d electrons must be paired internally. If the compound $ZrIr_3$ is formed, the Ir gives up electrons to approach the configuration d^5sp^2 while Zr gains electrons to approach the configuration d^4sp^2. If these configurations are attained, the number of electrons used for bonding is increased from the 25 bonding electrons of the pure elements to possibly as many as 31 bonding electrons per $ZrIr_3$.

For a given element on the left side of the periodic table, e.g. Zr, the number of electrons transferred and the increase in the number of bonding electrons should increase as one changes the other metal from Os, for example, to metals to the right. Thus the stability of their compounds should increase in the same direction. The decreasing internal pressures[3,10] as one moves to the right of Re also contributes to increasing stability of intermetallic compounds to a maximum at the tenth groups metals, Pd and Pt, with stability expected to fall off with decreasing internal pressures below that of Zr, and increasing promotion energies required for removal of d electrons. One would also expect a limit to the possible charge transfer.

Likewise, one would predict that with a given element on the right side of the transition series, e.g. Pt, stability of intermetallic compounds should increase as the other metal is changed from Mo, for example; to metals to the left. The stability of the intermetallic compounds is expected to reach a maximum in the fourth group where the internal pressures closely match those of Pd and Pt.

To test these predictions, the stabilities of transition metal compounds have been determined qualitatively by heating ZrC with Pt, Ir, and Os. A more detailed experimental account will be published. In each instance, the carbide was decomposed to form graphite and an intermetallic compound. Thus these intermetallic compounds of Zr have free energies of formation more negative than the -47 kcal/mole of ZrC which is one of the most stable carbides known. The compounds formed were the hcp $ZrPt_3$ with ordered $TiNi_3$ type structures, the ccp $ZrIr_{3-x}$ with ordered $AuCu_3$ type structure, and a hcp solution of Zr in Os.

In view of the extraordinary stability of these intermetallic compounds, a more drastic test of their stability was desired. The procedure of Bronger and Klemm[11] was applied by heating ZrO_2 in hydrogen at 1200°C. in the presence of Pt. Reduction took place to form $ZrPt_3$. The formation of $ZrPt_3$ and similar intermetallic compounds is undoubtedly the cause of the so-called "hydrogen embrittlement" of Pt-Rh thermocouples in oxide protection tubes under reducing conditions. To achieve reduction under these conditions, the thermodynamic activity of Zr may have been reduced by almost a factor of 10^{20} by alloying with Pt. The same principles can be used to explain the marked increase in melting point of Pt upon addition of 4th and 5th group metals.[12] The vacant d and p orbitals of Zr provide a sink for paired d electrons from Pt and thus make available all of the electrons for bonding. The same principles explain why transition metals to the right of Zr stabilize the bcc structure with the d^3s configuration compared to the hcp d^2sp configuration. Any transition metal with three or more unpaired d electrons would not be able to make as good use of these electrons when surrounded by d^2sp Zr atoms as when surrounded by d^3s Zr atoms. This is predicted by the Engel theory whether the metal added has bcc, hcp or ccp structure. Hume-Rothery's footnote (Pg. 1042) that claims that the theory predicts stabilization of a structure only by metals of the same structure represents a miscomprehension of the application of the theory.

I am sorry that Professor Hume-Rothery reacted so hastily to the manuscript which I sent him. I hope that he will take the time to carefully examine reference 3 including the discussion. He will be delighted to find that a full understanding of the application of the Engel correlation makes it possible to extend the application of the Hume-Rothery Rules by more than an order of magnitude to include both transition and non-transition metal systems.

References

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3. L. Brewer, "Prediction of High Temperature Metallic Phase Diagrams," Chapter 2, pgs. 12-103 of High-Strength Materials, Proceedings of Second Berkeley International Materials Conference, June 1964, Edited by V. F. Zackay, John Wiley, N.Y., London, 1965.
4. Reprints of reference 3 were not provided. In view of the expense of photo-duplication of a paper of this length, I regret that I am unable to meet the many reprint requests that have been stimulated by Professor Hume-Rothery's paper.
5. L. Brewer, paper to be presented at the March 1966 Colloquium on Phase Stability in Metals and Alloys at Geneva, Switzerland.
6. C. E. Moore, Atomic Energy Levels, Vol. 1-3, U.S. Government Printing Office, Washington, D.C., 1949, 1952, 1958.
7. J. C. Jamieson and A. W. Lawson, J. Appl. Phys., 33, 776(1962). The recent work of F. A. Bundy, J. Appl. Phys., 36, 616(1965) fixes the volume change for bcc to hcp Fe at -0.275 cc/mole at the transformation pressure of 110 kilobars at 490°C and reference is made to X-ray data fixing ΔV at -0.30 cc/mole at low pressure. Thus hcp Fe

is metastable by less than 1 kcal in confirmation of the predictions of the Engel correlation.

8. M. Hansen and K. Anderko, *Constitution of Binary Alloys*, McGraw-Hill, New York, 1958.

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10. J. H. Hildebrand and R. L. Scott, *Solubility of Nonelectrolytes*, 3rd. Ed., Reinhold, N.Y., 1950 and *Regular Solutions*, Prentice-Hall, Englewood Cliffs, N.J., 1962.

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12. *WARNING*. A note of caution should be included in regard to preparing large samples of these abnormally stable intermetallic compounds by direct reaction of the elements. The heat evolutions are so large that temperatures over 3000°C. will result if an adiabatic reaction is initiated by heating to around 1000°C. A private communication from Professor John Margrave reports an explosion resulting from the reaction of Hf with Pt during experiments which confirmed the high stability of $HfPt_3$ predicted by the Engel theory.

Figure Caption

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

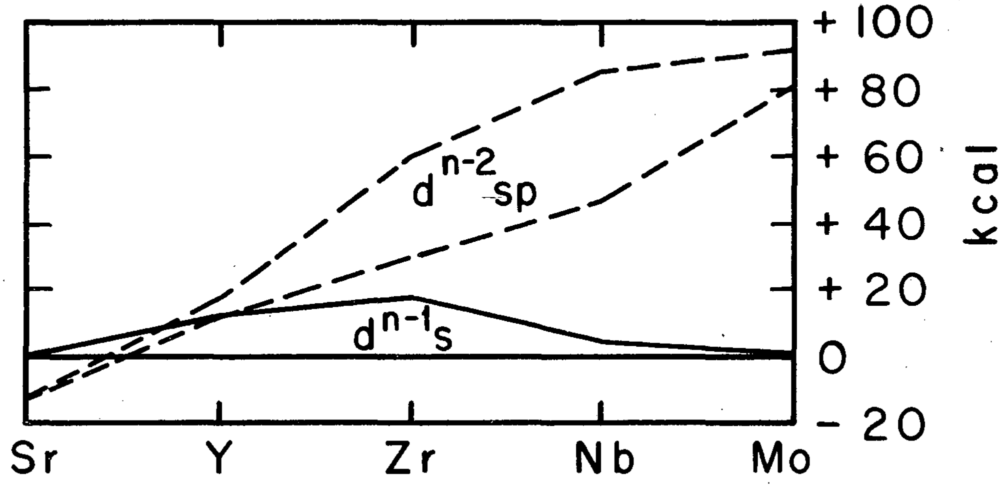

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Fig. 1